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APPLICABILITY OF CATALYTIC OXIDATION TO THE DEVELOPMENT OF NEW PROCESSES FOR REMOVING SO_2 FROM FLUE GASES

Volume II – EXPERIMENTAL PROGRAM

Contract No. PH 22-68-12

Prepared by

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National Air Pollution Control Administration
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U.S. Public Health Service
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During the first phase of this project, which covered the identification and evaluation of existing and potential methods of applying catalysis to the oxidation and removal of SO_2 from power plant stack gas, a large quantity of information and data was accumulated and assessed. This evaluation revealed the need for laboratory verification of the published data on promising oxidation systems. This volume presents subsequent data and information generated in the laboratory and on the drawing board.

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APPLICABILITY OF CATALYTIC OXIDATION TO THE DEVELOPMENT OF NEW PROCESSES FOR REMOVING SO_2 FROM FLUE GASES

Volume II - Experimental Program

Contract No. PH 22-68-12

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Submitted to

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U.S. Department of Health, Education, and Welfare
5710 Wooster Pike
Cincinnati, Ohio 45277

FOREWORD

The intent of this volume is to present in an organized manner the accumulation and assessment of all experimental and design work accomplished during the execution of Contract PH 22-68-12 by Monsanto Research Corporation, Dayton, Ohio. In that this volume represents the second phase of a three-phase program of concurrent tenure, occasional reference to phases I and III may be seen at various points through the text. Further definition of these areas may be found in the respective volumes, each of which is reported under separate cover.

This final report is presented in three volumes in an effort to make the material accessible on the assumption that it is of practical value and therefore will be put to use.

Volume I is intended to contain all, and only, that material derived from, or related to, the literature search. Essentially all information in Volume I is directly based on the literature.

Volume II presents data and information generated in the laboratory and on the drawing board.

Volume III is an indexed bibliography.

Finally, guidance through the three volumes is offered in the form of the Foreword, Project General Summary and Tables of Contents in each of the three volumes.

The authors wish to acknowledge the many helpful comments and suggestions of the NAPCA Project Officer, Mr. George L. Huffman.

PROJECT GENERAL SUMMARY

The salient features of the project are summarized briefly below. Expansion and details are given in the texts of Volumes I and II.

The main objectives of the program were:

a. Search all available literature for pertinent information relative to the catalytic oxidation of sulfur dioxide, i.e., active materials, mechanisms of catalysis, methods of application, equipment employed, etc. Identify, describe and evaluate processes disclosed in the literature to have commercial potential for removal of sulfur dioxide from flue gas by oxidation.

b. Test, in the laboratory, candidate materials and methods suggested in the literature for potential application to removal of sulfur dioxide from flue gas by catalytic oxidation.

c. Identify at least one effective catalyst for the desired application and design a process for removal of sulfur dioxide from flue gas by catalytic oxidation and recovery of the sulfur value.

An intensive search of the literature revealed the following:

a. The transition metal oxides, notably vanadia, and platinum were the most commonly employed solid catalysts for practical conversion of sulfur dioxide to trioxide. Nitrogen dioxide was the only practical gaseous catalyst noted.

b. Kinetic equations describing conversions of sulfur dioxide over vanadia or platinum catalysts were derived from data relative to commercial production of sulfuric acid, i.e., high concentrations of sulfur dioxide. There was nothing available to describe results at the comparatively low concentrations of sulfur dioxide found in flue gas.

c. A number of processes were described as having commercial potential for flue gas cleaning. Comparative cost-performance evaluation of these oxidation processes eliminated all but two types as having realistic commercial potential, viz., one type based on vanadia catalyst and one based on nitrogen dioxide catalyst.

d. The most practical mode of recovery of oxidized sulfur value from a use standpoint, in this country, is production of fertilizer grade sulfuric acid.

Laboratory tests and comparative evaluation of commercial and experimental catalysts indicated the following:

a. Commercial vanadia catalysts employed in production of sulfuric acid are effective in converting sulfur dioxide at concentrations found in flue gas.

b. Although platinum catalyst performance is essentially equivalent to that of vanadia, a cost-performance comparison indicated vanadia is ten times more effective.

c. No other candidate materials were shown to be as effective as vanadia, platinum or nitrogen dioxide in converting sulfur dioxide to trioxide.

d. Nitrogen dioxide was the only practical "low temperature" catalyst observed.

e. Using nitrogen dioxide as a catalyst, it is potentially practical to remove both sulfur dioxide and indigenous nitrogen oxides from flue gas simultaneously.

From preliminary process designs and cost estimates, based on laboratory data generated in this program, the following emerge:

a. Processes, based on vanadia catalyst, for oxidizing sulfur dioxide and removing it from power plant flue gas, as sulfuric acid, are likely to cost in the range of $12 to $25 of capital per installed Kw of power plant capacity. A large portion of the cost results from the need for corrosion resistant equipment.

b. Operating costs for vanadia based processes are likely to be in the range of 0.50 to 0.74 mills/Kw-Hr generated before sulfur value net back.

c. A substantial reduction in capital and operating costs are potentially available through a technique of sorbing the oxidized product gas from the main flue gas stream and recovering it separately.

d. The vanadia based processes are better suited to proposed new power plant installations than to existing plants because of numerous difficulties in retro-fit to existing power plants.

VOLUME II

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VOLUME II SUMMARY

During the first phase of this contract, which covered the identification and evaluation of existing and potential methods of applying catalysis to the oxidation and removal of SO_2 from power plant stack gas, a large quantity of information and data was accumulated and assessed. This evaluation revealed the need for laboratory verification of the published data on promising oxidation systems. While the literature noted a large number of individual materials, and combinations of materials, as being capable of converting SO_2 to SO_3, the experimental conditions, conversion efficiencies, and extrapolated economics cited for nearly all cases were impractical with respect to the flue gas application.

Essentially all these studies were related to conversion with vanadia-based catalyst in gas streams containing 5-12% SO_2, typical of that in contact with sulfuric acid plant operation. Accordingly, it became necessary to provide laboratory verification of these data under simulated flue gas conditions.

Commercially available catalysts were tested over a broad range of conditions, resulting in the conclusion that vanadia-based materials were the only practical compositions presently available with the capability to remove SO_2 from power plant flue gas under normal operating conditions.

A large number of potentially promising experimental compositions were tested, but none was found which exhibited properties superior to that of commercial vanadia-based catalysts for the pertinent task. During this experimental investigation enough promising data was gathered to merit further research in the area of new catalysts which would operate at a lower temperature than those presently available.

The development of a process which will simultaneously remove both SO_2 and NO_x was implemented experimentally as a logical outgrowth of the experimental program. A detailed description of this process has been included in the text (Section V). As this process bears some similarity to the Tyco removal process, a comparison between the two is also shown.

Preliminary catalytic oxidation process designs were developed for application to a large new power plant facility, a large existing power plant facility, a small existing power plant facility, and a new smelter facility. These designs include estimates of investment and operating costs. Since a great deal of data was obtained during the execution of the experimental and design phases of the program, most of it has been relegated to an appendix section at the back of the volume.

VOLUME II CONCLUSIONS

1. Vanadia catalysts available for commercial production of sulfuric acid are effective in converting SO_2 in flue gas to SO_3.
2. Platinum catalysts available for commercial hydrocarbon reforming are effective in converting SO_2 in flue gas to SO_3.
3. Although platinum catalyst is essentially equivalent in performance to vanadia catalyst, it is an order of magnitude more expensive.
4. The presence of NO_x in the flue gas stream had no apparent effect on catalyst conversion efficiency.
5. No catalyst compositions tested, other than platinum and vanadia based compositions, were deemed satisfactory because of their instability to either SO_2 or SO_3.
6. No other combination of catalyst-promoter tested was as effective as the vanadia-based compositions for oxidizing SO_2 to SO_3.
7. Catalytic oxidation processes are better suited to new plant design because of high costs associated with retro-fit into existing power station designs.
8. Fleeting evidence in support of a proposed mechanism in the literature for vanadia catalysis, was obtained experimentally.
9. No low temperature catalyst, other than nitrogen dioxide, was found during the experimental search - however, enough evidence was gathered to merit further investigation into low temperature, solid catalysts.

INTRODUCTION

The theories and principles of catalysts are discussed in Volume I of this report. The most significant conclusion emerging from the discussions in Volume I was that heterogeneous catalysts by vandaia is the most effective means of converting SO_2 to SO_3. This statement, however, does not specify a formulation of vanadia mixed with anything else and does not suggest, in itself, how the vanadia is contacted with the sulfur dioxide. Furthermore, there were, in the literature, several strong indications, or leads, to potentially new catalysts that might operate at lower temperatures, or that might be more active per unit weight.

The experimental effort, then, had two major objectives: (1) to seek "low" temperature or more active catalysts and (2) to define at least one catalyst around which a process could be designed for removing SO_2 from power plant stack gas.

In the following discussion, it is helpful to understand the general terminology and structure of solid catalysts. The basic parts of a solid catalyst consist of:

1. Catalyst - active material, usually noble metals or transition metal oxides.
2. Promoter - usually an inorganic salt or salt mixture that enhances the activity of the catalyst.
3. Support - an inert material such as Fuller's earth or alumina used to provide bulk to the mixture and increase surface area.

The relative proportions of the three materials are by no means fixed but fall, roughly, into the following ranges, by weight:

Catalyst - <1% to ~10%

Promoter - ~20% to ~30%

Support - ~70% to ~80%

There are numerous methods for constructing a solid catalyst. The final form is usually that of a pellet of various shapes and sizes when it is to be used in a fixed bed contactor. For fluidized bed contacting, the catalyst is produced in powder form to various degrees of fineness.

The ingredients can be combined by:

1. Dry mixing, pelletizing, calcining.
2. Adding enough liquid to make a dough and extruding pellets, drying, calcining.
3. Dry mixing catalyst and promoter, calcining, grinding the "clinker", dry mixing with support, pelletizing.
4. Impregnating support with a solution of catalyst and promoter, drying, pelletizing, calcining.

It may not always be required to calcine. When it is necessary, however, the purpose is usually to convert the catalyst-promoter mixture to the optimally active composition. For example, the desired composition of the promoter in a vanadia catalyst is the pyrosulfate, whereas the promoter may initially be added as the sulfate.

The number of permutations and combinations of catalyst pretreatment operations promotes the impression that the field of catalysis is a "black art".

I. EXPERIMENTAL EQUIPMENT

A. Catalyst Test Unit

The system that was designed and fabricated for the purpose of testing catalysts consists of the following functional sections:

- Preparation and metering of simulated flue gas
- Temperature control
- Reactor
- Analysis

Figure 1 is a schematic flow diagram of the test stand. Figure 2 is a view of the control panel.

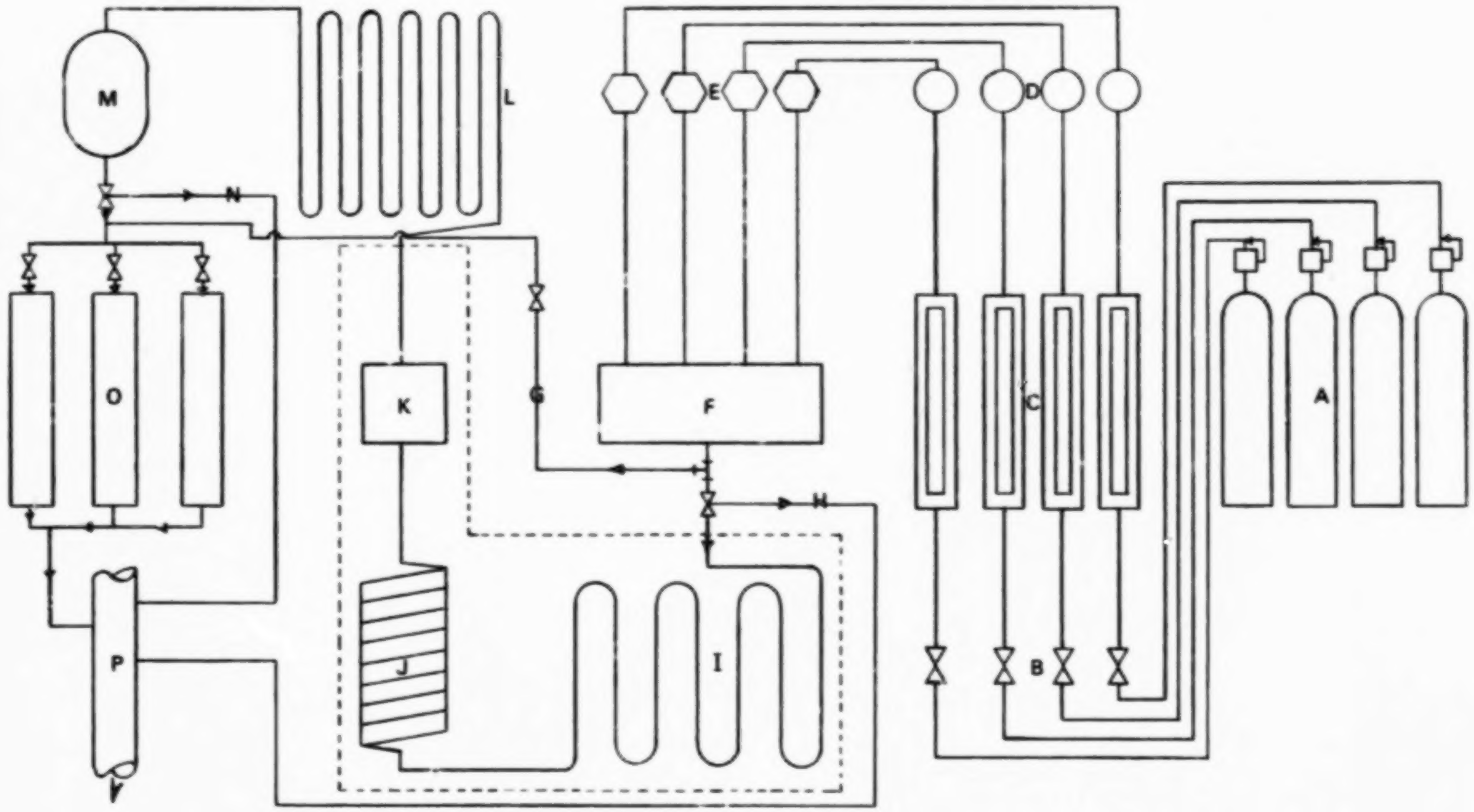
The gas preparation section is designed to permit mixing and feeding of simulated flue gas from cylinders, including calibrating gas mixtures. Precise flow control is necessary here, and is provided through multistage pressure regulation, precise flowmeters, and very sensitive flow controllers.

The sample gas flow-control subassemblies, as shown in Figure 3, consist of two-stage regulation at the cylinder source followed by rotameters with needle valve control. Flow controllers are installed downstream of the rotameters and are designed to control from constant upstream pressure sources through variable downstream pressure sources. The flow rate set point is manually set by adjusting an external valve handle. This valve acts as a variable orifice to provide a pressure drop across the high and low pressure chambers of the diaphragm. If the pressure drop changes due to a change in supply or outlet condition, the diaphragm will change to the operating point of an internal throttling valve to re-establish the pressure drop across the manual valve. The flow control system has the capability of metering individual component flows as well as multicomponent flows. In the case of individual component flow, the components are mixed downstream of the flow metering assembly through a specially designed mixing chamber.

B. Temperature Control

The mixed gas stream next passes through a section of preheated line prior to entrance into the reactor section. In the reactor section, the gas is heated even further in an eight foot coil within the

Figure 1. Test Unit Schematic Flow System



A. Gas Bottles
B. Flow Control Valves
C. Flow Meters
D. Pressure Gauges
E. Flow Controllers
F. Mixer
G. Inlet Gas Sample
H. Reactor Bypass
I. Preheat Section
J. Furnace Preheat Section
K. Catalyst Bed
L. Process Stream Cooler
M. Condensables Trap
N. Process Stream Vent
O. Process Stream Analyzer
P. Exhaust Stack

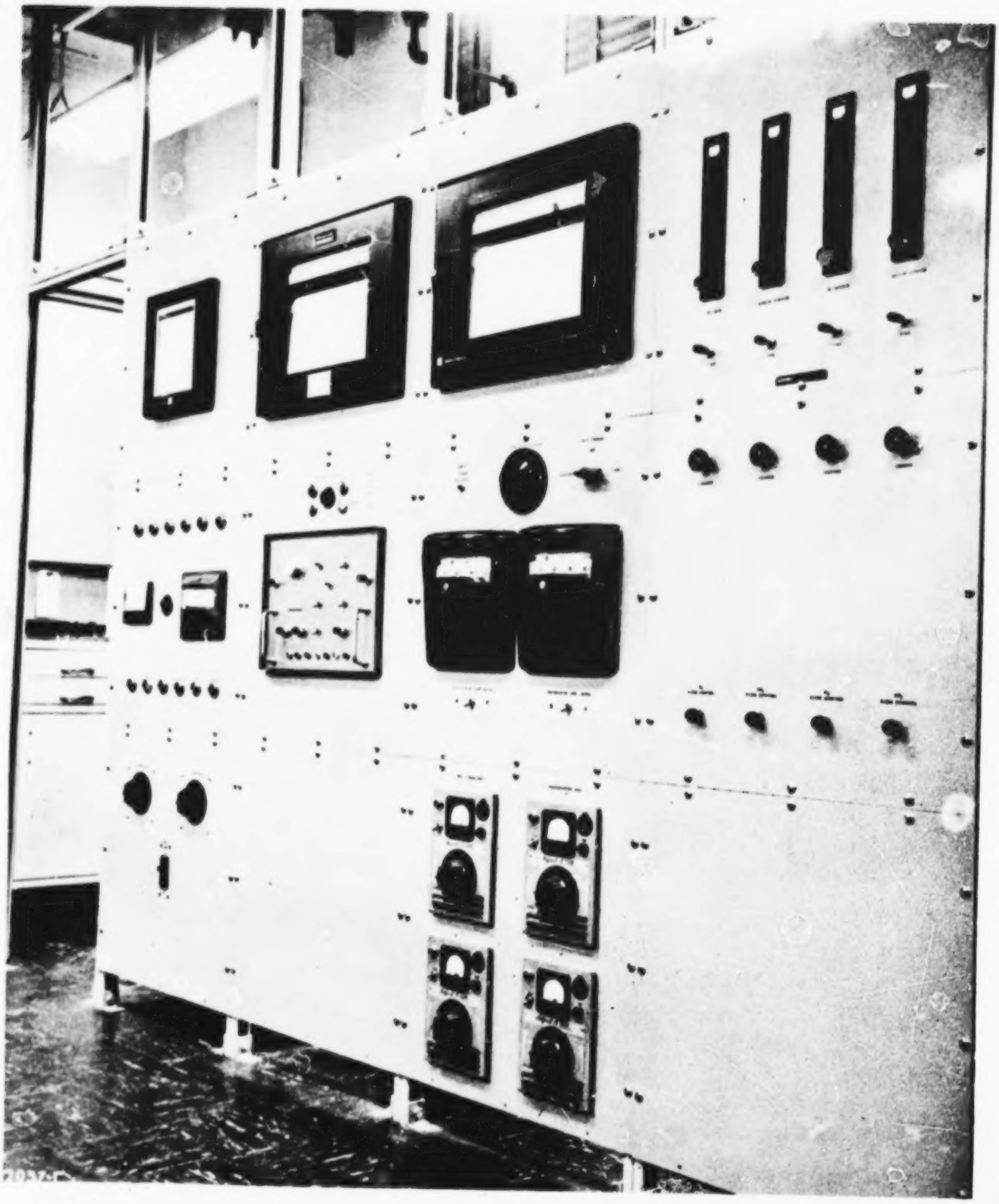


Figure 2. View of Test Unit Control Panel

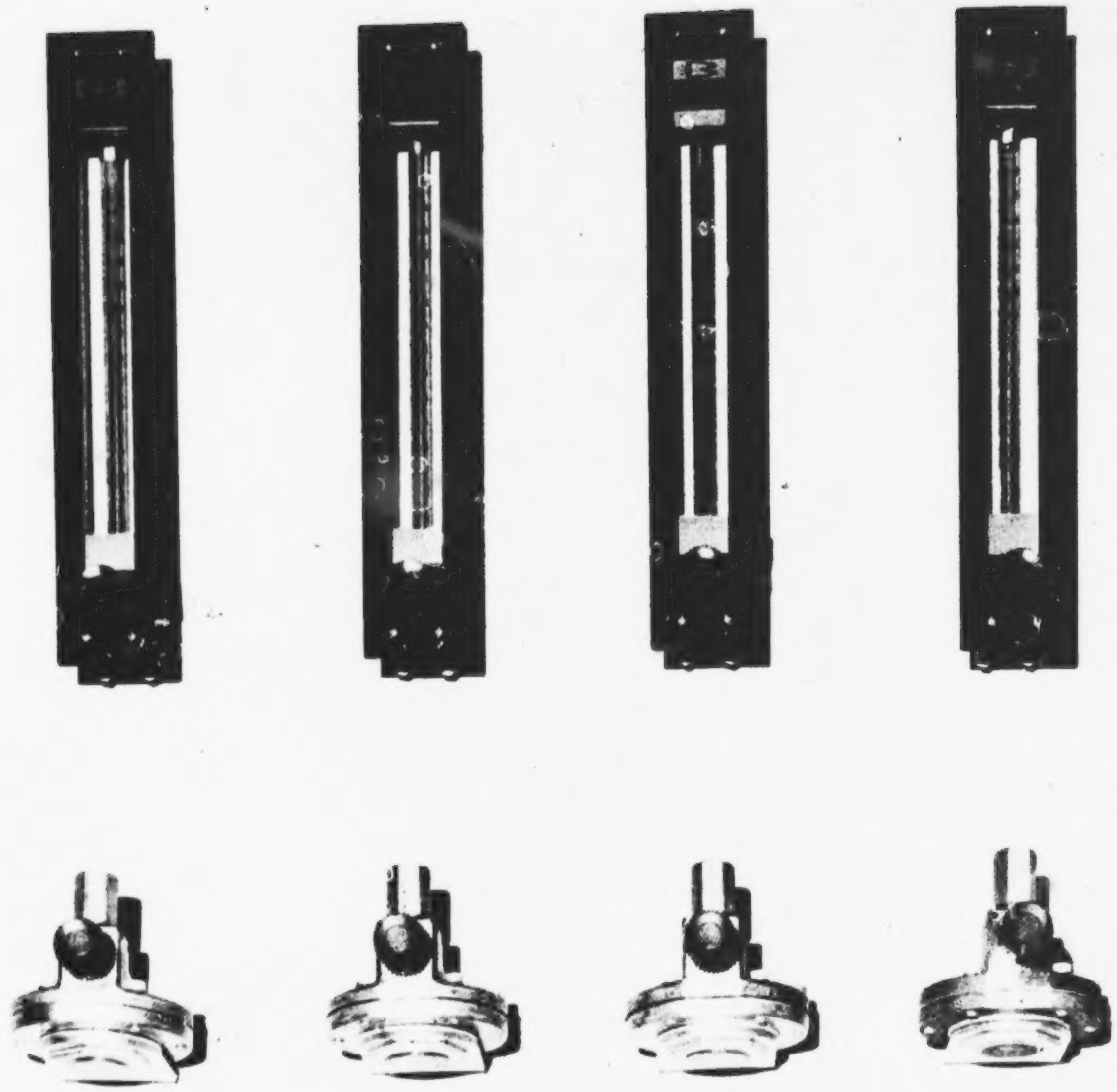


Figure 3. Flow Controls

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reactor furnace enclosure. Thermal input is controlled by two 220-volt, 3-phase Variacs, one 3-phase contactor and a West temperature controller, allowing exact adjustment of input power and temperature control within ±1°F. Figure 4 shows the temperature control assembly.

C. Reactor

Gas from the flow control system enters the reactor, Figure 5, through an eight-foot spirally-wound heating section ahead of the reaction tube. The hot gas then flows through the catalyst bed and out the exit arm. Figure 6 shows an enlarged schematic of the catalyst bed, thermocouples and supporting assembly, all of which may be positioned in, or removed from, the reactor as one unit, allowing practical interchange of catalyst beds. Figure 7 details the reactor-assembly furnace-enclosure. The enclosure is mounted on a 3/4-inch, 100-lb steel plate which serves as a basic mounting surface as well as providing stability through a low center of gravity. A high-temperature blower extends through the base plate and into a stainless steel tank 12 inches in diameter and 24 inches in length. Within this tank, twelve 500-watt, high-temperature, strip heaters form an annulus surrounding the glass reactor tube and provide an 18-inch heated zone along the length of the reactor and preheat assemblies. Enclosed in a squirrel cage housing, the fan blade exhausts up the outside of the heat bank, and intakes along the center axis, providing a uniform thermal environment for the catalyst bed. The primary tank enclosure is surrounded by a minimum of three inches of FIBERFRAX ceramic insulation contained by a 30-gallon steel drum mounted on the base plate. Components of the reactor section are shown in Figures 8, 9 and 10.

D. Analysis System

The analytical system consists of an automatic, chromatographic process stream analyzer. The analyzing system has the capability to resolve accurately SO_2, O_2, and CO_2, with a multistage range selector for SO_2, to encompass 0-0.2%, 0-0.4%, and 0-5% of this component. Other ranges are easily incorporated with the addition of modular, attenuator cards in the system programmer.

The complete analyzing system consists of four major units: sample conditioner, analyzer, programmer, and read-out device consisting of an L&M series H recorder.

The sample conditioner receives the raw sample from the process stream and prepares it for introduction into the analyzer. The chromatographic analyzer separates the sample into its individual constituents and, as they elute, transmits signals to the programmer. Signals are proportional to the concentrations of the various components. The analyzer utilizes a thermal conductivity detector with four filaments.

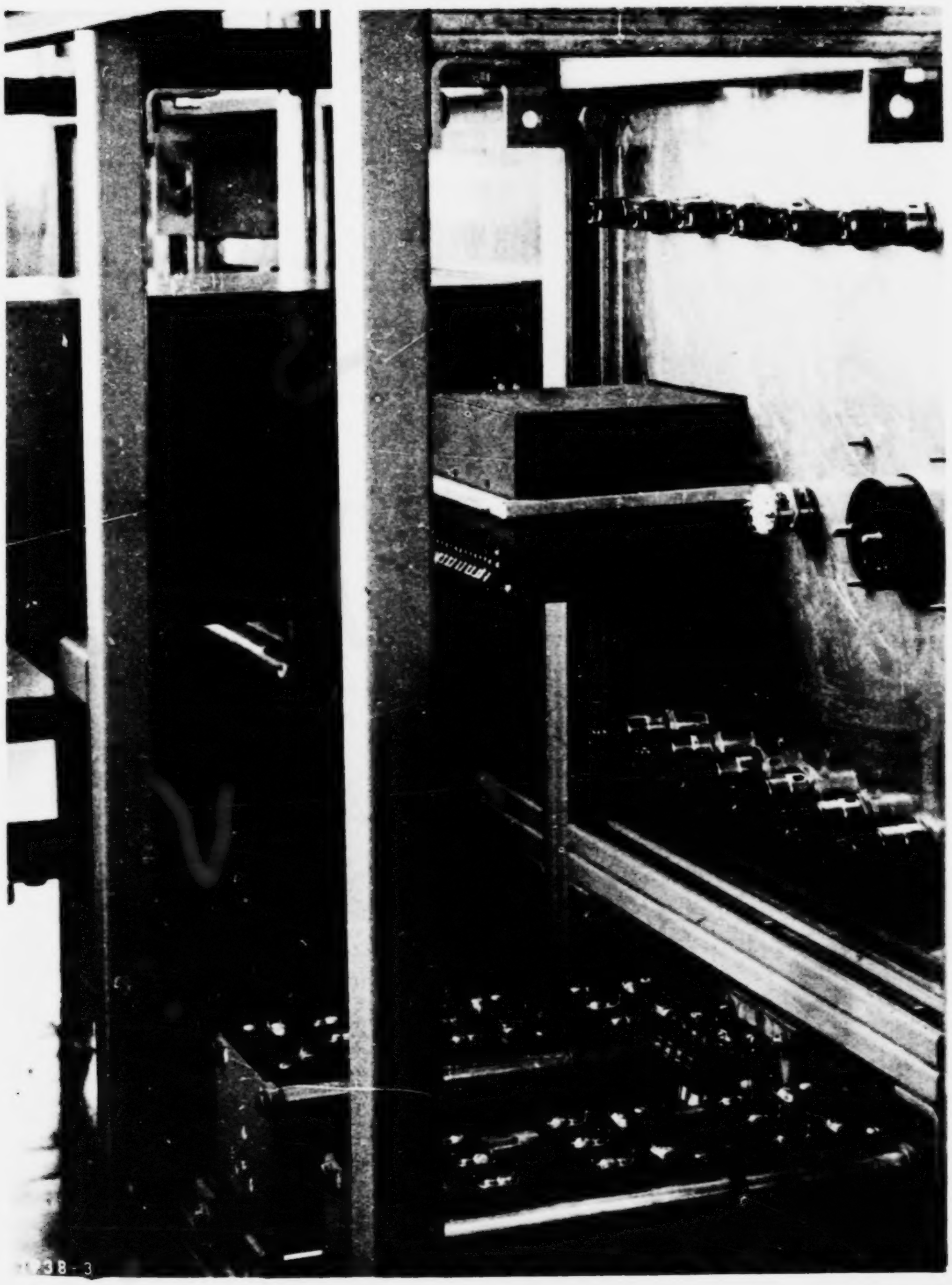

Figure 4. Reactor Furnace Controls

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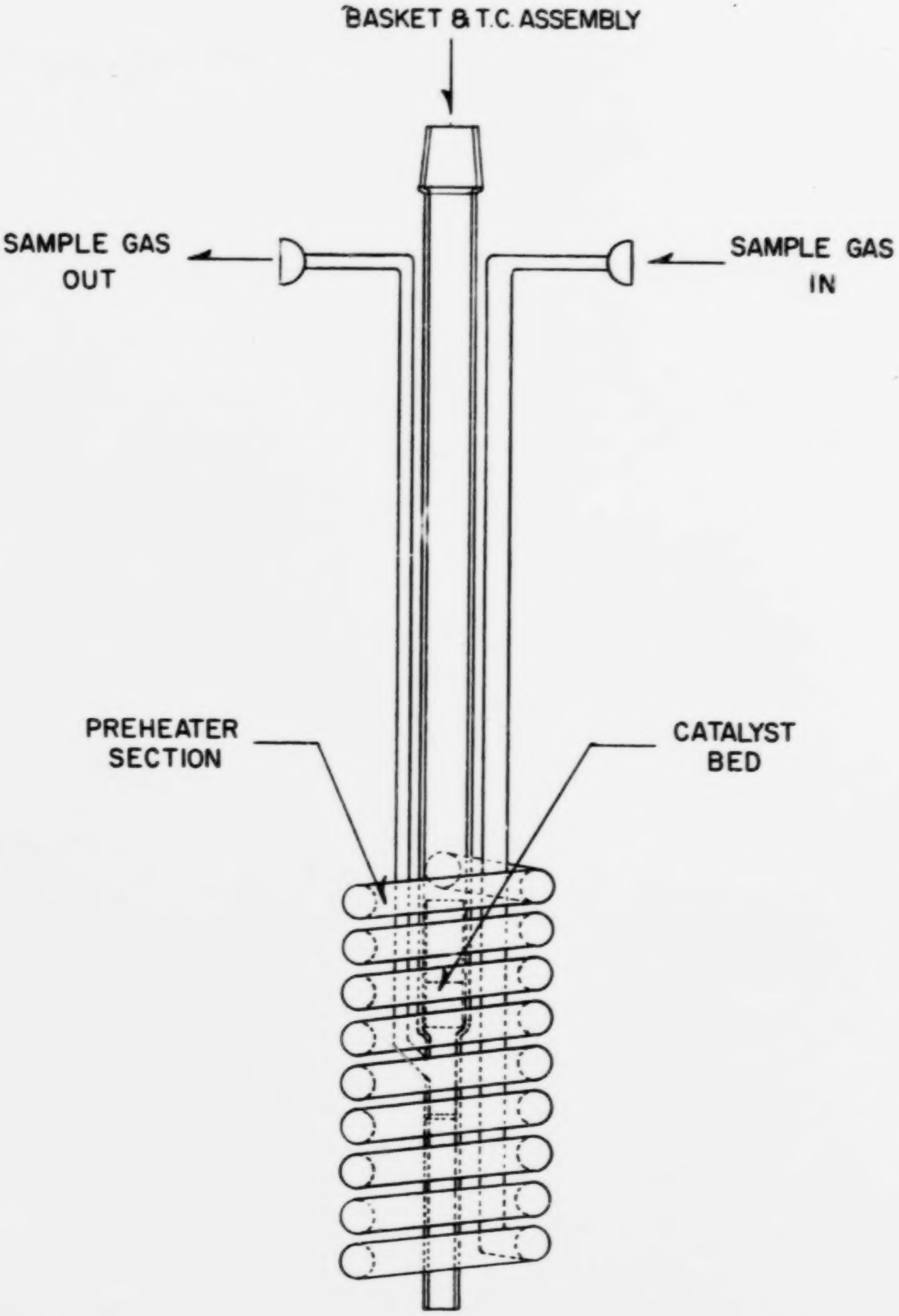
BASKET & T.C. ASSEMBLY
SAMPLE GAS OUT
SAMPLE GAS IN
PREHEATER SECTION
CATALYST BED

Figure 5. Glass Reactor and Preheater Section

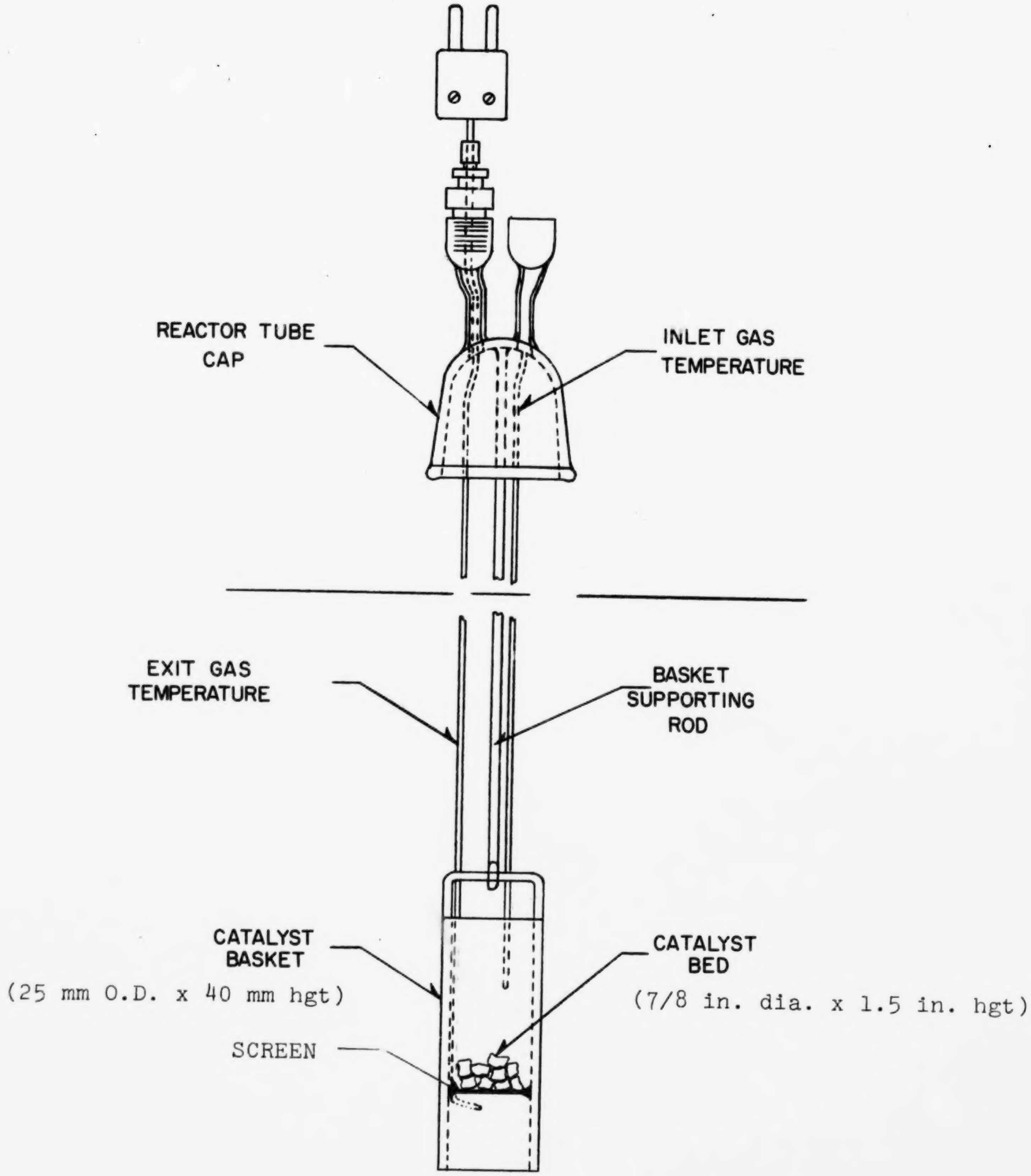
REACTOR TUBE CAP
INLET GAS TEMPERATURE
EXIT GAS TEMPERATURE
BASKET SUPPORTING ROD
CATALYST BASKET
(25 mm O.D. x 40 mm hgt)
CATALYST BED
(7/8 in. dia. x 1.5 in. hgt)
SCREEN

Figure 6. Catalyst Bed and Temperature Sensing Assembly

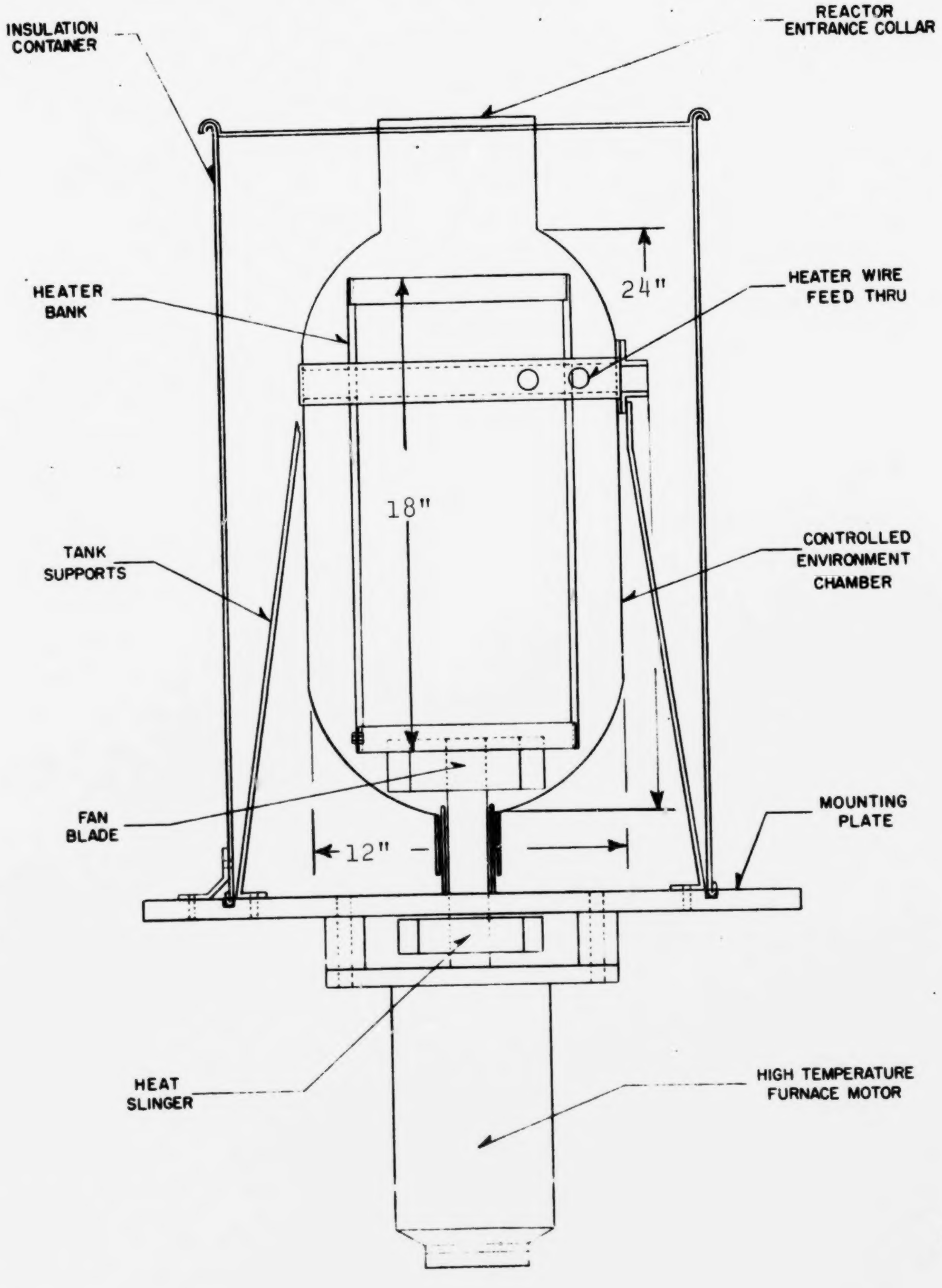
INSULATION CONTAINER
REACTOR ENTRANCE COLLAR
HEATER BANK
24"
HEATER WIRE FEED THRU
18"
TANK SUPPORTS
CONTROLLED ENVIRONMENT CHAMBER
FAN BLADE
12"
MOUNTING PLATE
HEAT SLINGER
HIGH TEMPERATURE FURNACE MOTOR

Figure 7. Reactor Furnace Enclosure

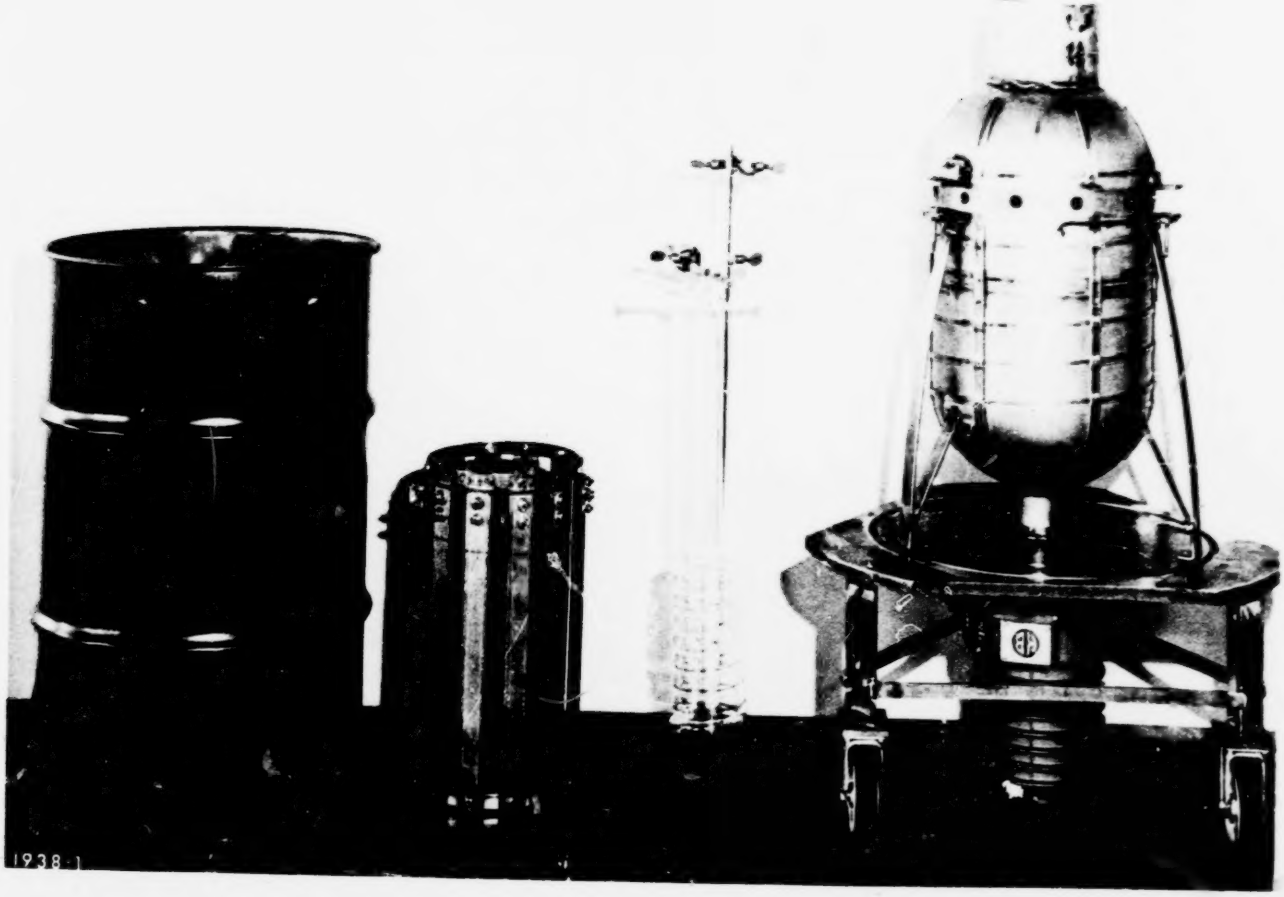

Figure 8. Reaction Section Components

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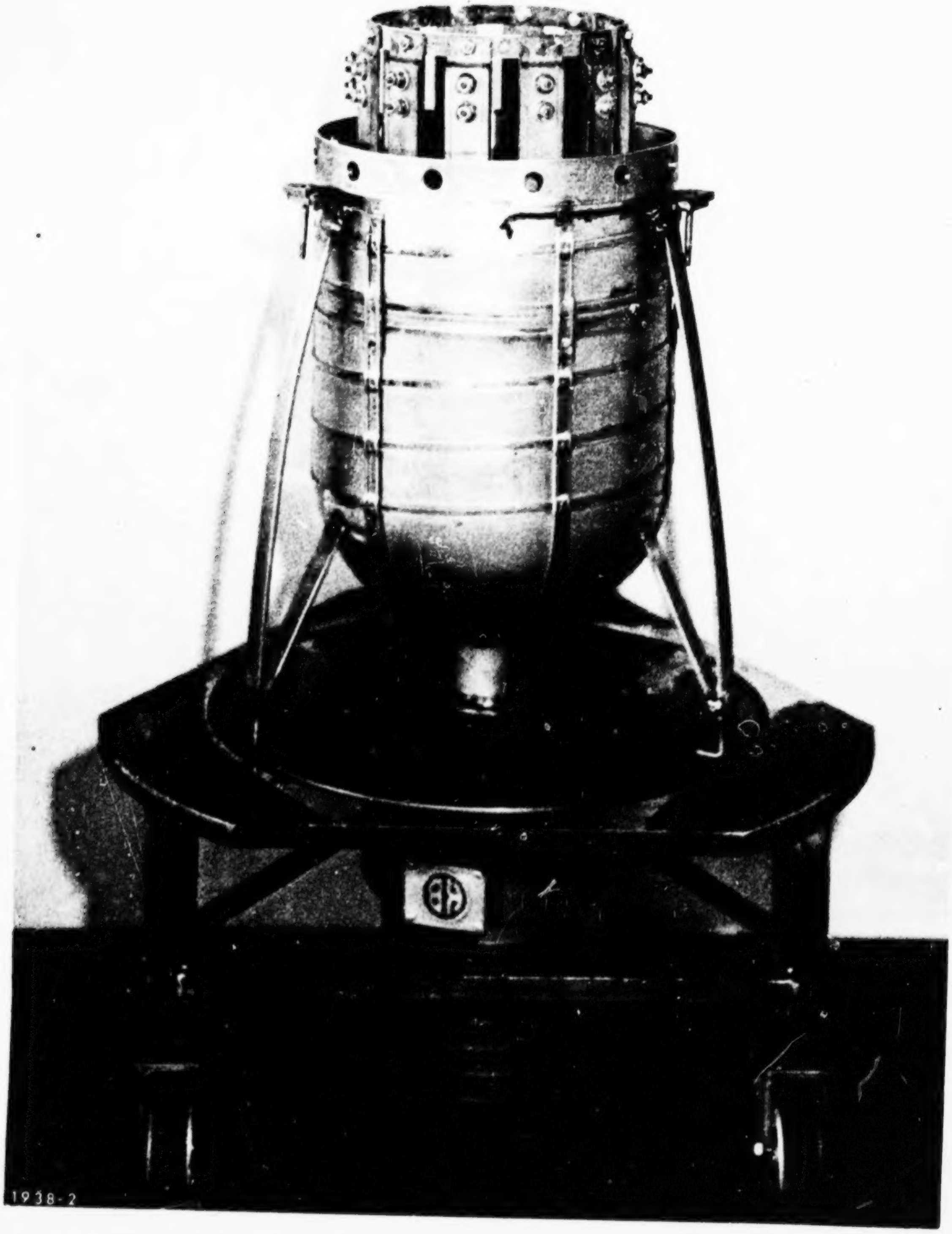

Figure 9. Furnace Sub-assembly

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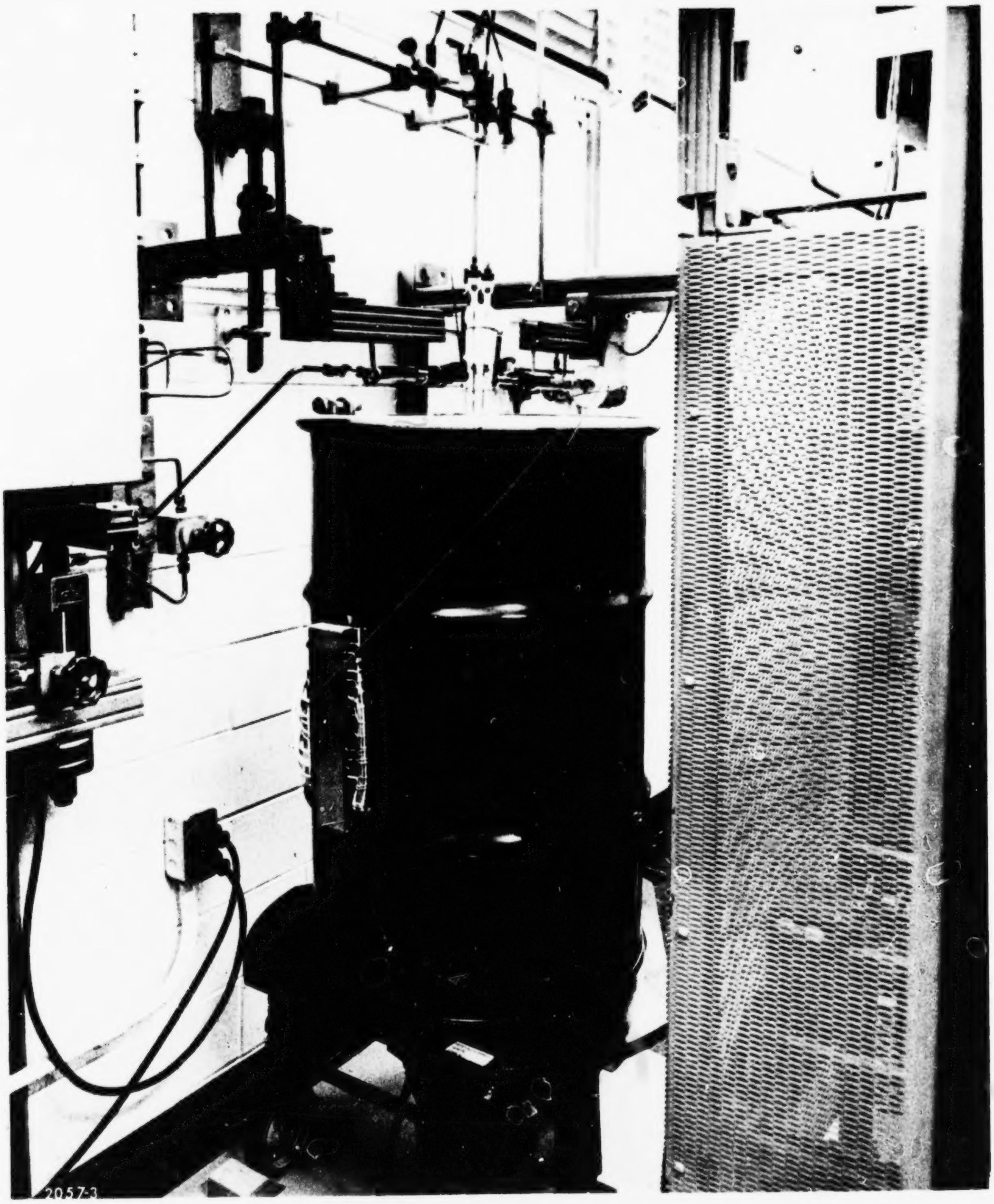


Figure 10. Reactor and Furnace Enclosure

NOT REPRODUCIBLE

The programmer provides the control signals required to operate the analyzer, and converts the analyzer-output signal into a form compatible with the read-out device. The sampling programs offered are:

- Reactor inlet/outlet, sequential, iterative
- Iterative inlet only
- Iterative outlet only
- Manual select

Various components of the analytical system are shown in Figures 11 through 13.

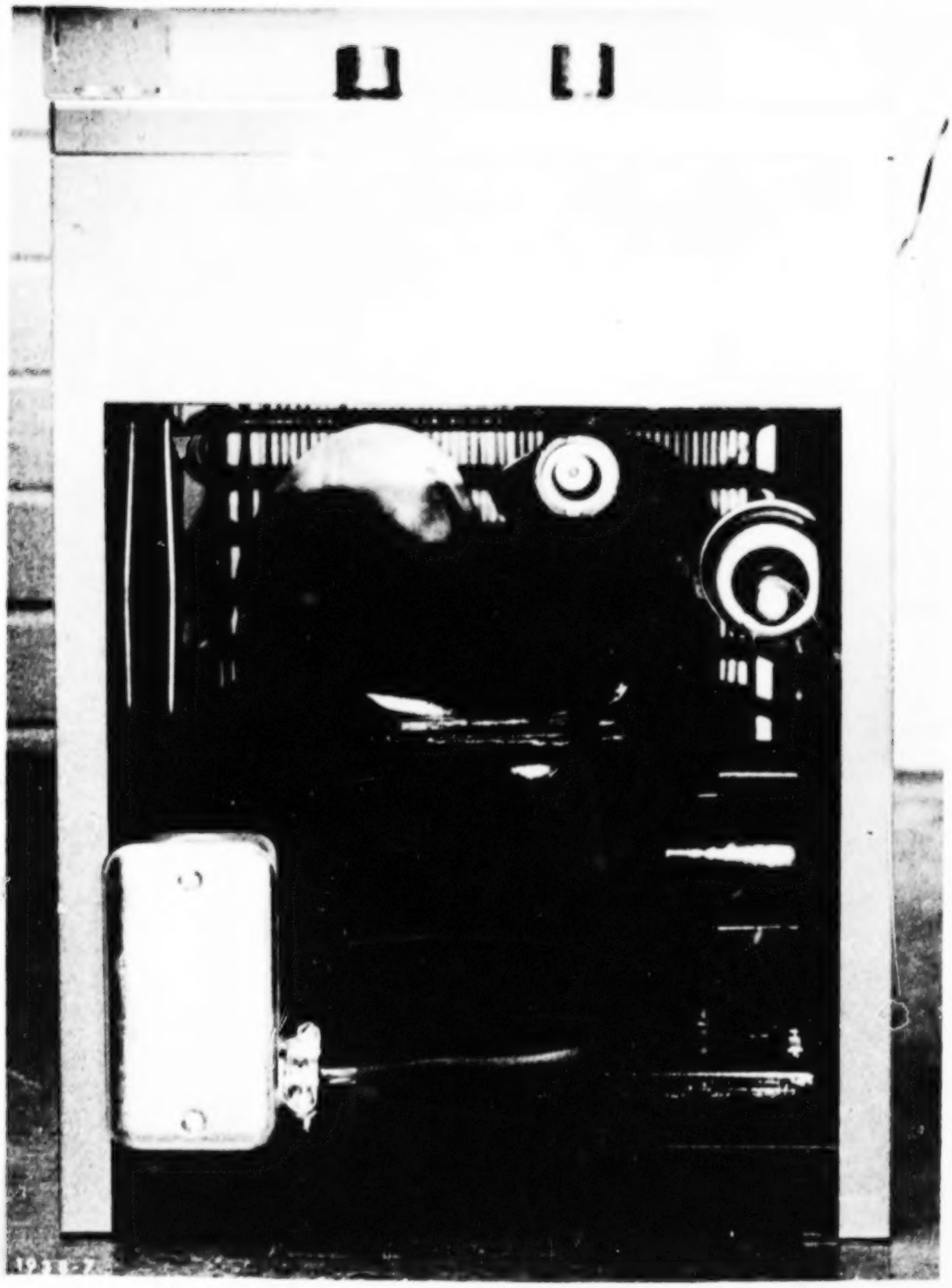


Figure 11. Process Stream Cooler Between Reactor and Chromatograph

NOT REPRODUCIBLE

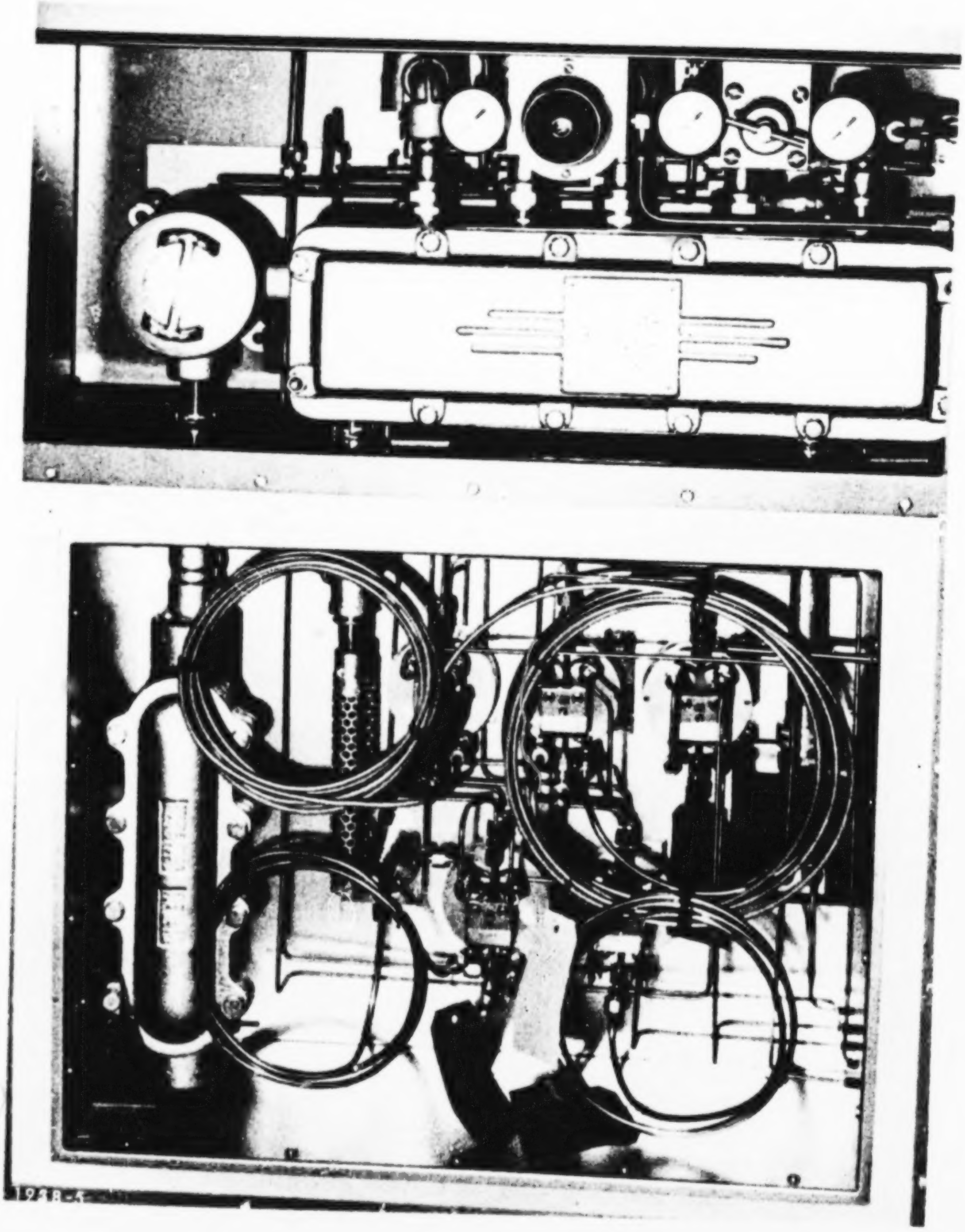


Figure 12. Process Stream Analyzer

NOT REPRODUCIBLE

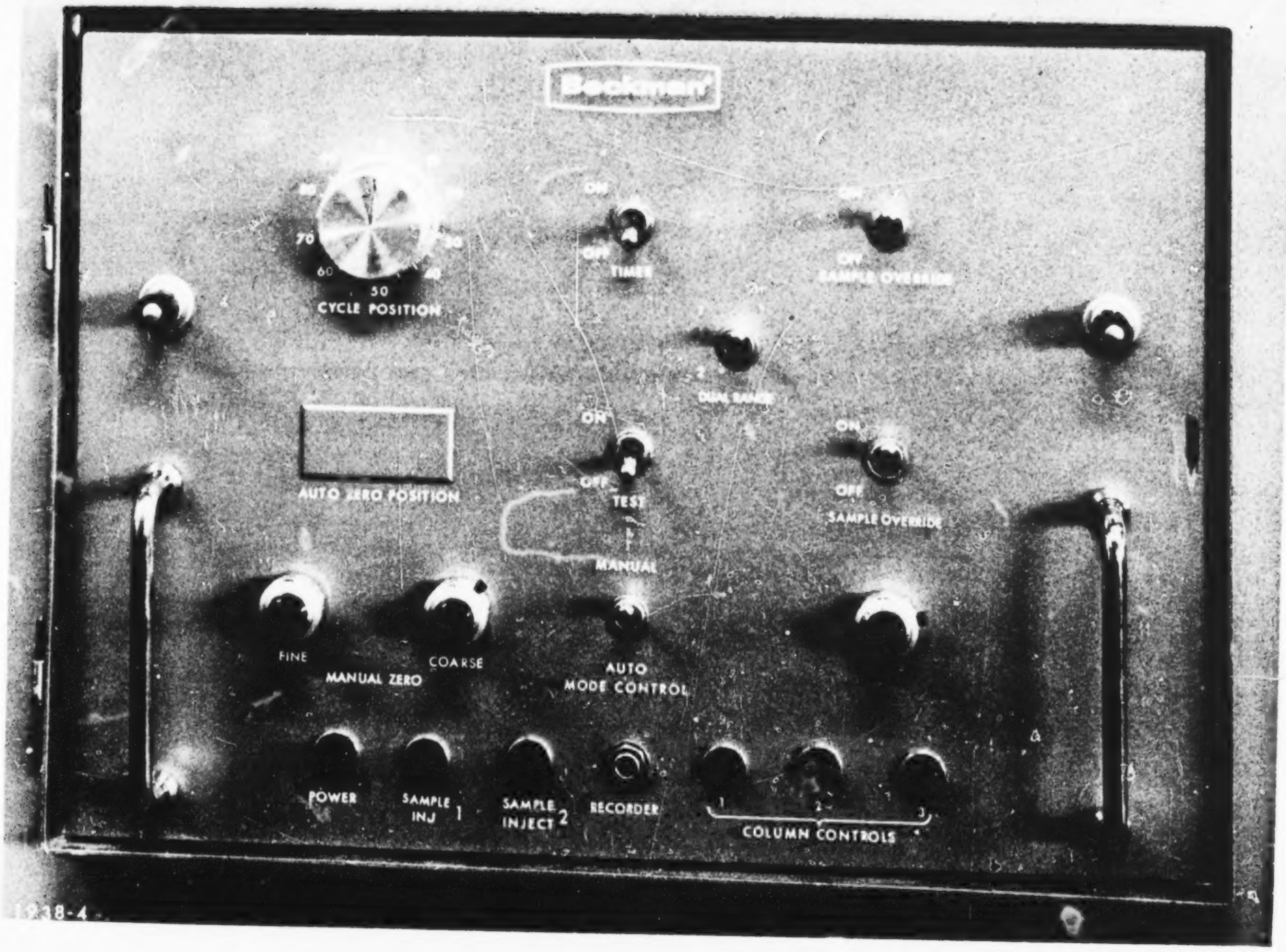

Beckman
70
60
50
CYCLE POSITION
ON
OFF
TIMER
ON
ON
SAMPLE OVERRIDE
2
DUAL RANGE
AUTO ZERO POSITION
ON
OFF
TEST
ON
OFF
SAMPLE OVERRIDE
MANUAL
FINE
COARSE
MANUAL ZERO
AUTO
MODE CONTROL
POWER
SAMPLE INJ 1
SAMPLE INJECT 2
RECORDER
1
2
3
COLUMN CONTROLS
1938-4

Figure 13. Analysis System Programmer

NOT REPRODUCIBLE

II. CATALYST PREPARATION

Laboratory equipment obtained for catalyst preparation included a large capacity oven (0-300°F) for drying samples, a small high-temperature furnace (0-1830°F) for calcining operations; and a pelletizing press (Manesty), Figure 14.

The primary method of sample preparation employed in catalyst studies consisted of the following:

- Weigh out constituents in fine powder form (pregrind if necessary)
- Homogeneously dry mix constituents
- Bake mixture overnight to remove free water
- Pelletize
- Calcine

The support material most commonly used was calcium montmorillonite, or Fuller's earth. It was checked for its capacity to retain molten alkali salts (promoters) by preparing a blend of it with, for example, potassium bisulfate (20% by weight), crushed to approximately 300 mesh. This blend was then pelletized and heated in a furnace 120°F above the normal melting point of the $KHSO_4$. Subsequently, the pellets were removed and examined under magnification, for signs of running or sweating of the $KHSO_4$.

In Figure 15, obtained with the aid of the scanning electron microscope, the upper photograph (6000X) shows the surface of a catalyst pellet before calcining. The large particles, roughly 3 microns in size, are, we believe, the mixture of catalyst and promoters. The smaller particles can clearly be identified as diatomaceous earth, the support. The surface exposed to gaseous reactants is highly irregular and the pores exist as the space between or within the particles.

The lower photograph (6000X) in Figure 15 shows the surface of a pellet after calcining at 800°F. The large particles are absent and the support material appears to have been rather uniformly coated, presumably by the molten promoters in which the catalyst is dispersed.

In some preparations, alumina was employed as support in a manner similar to that for Fuller's earth.

NOT REPRODUCIBLE

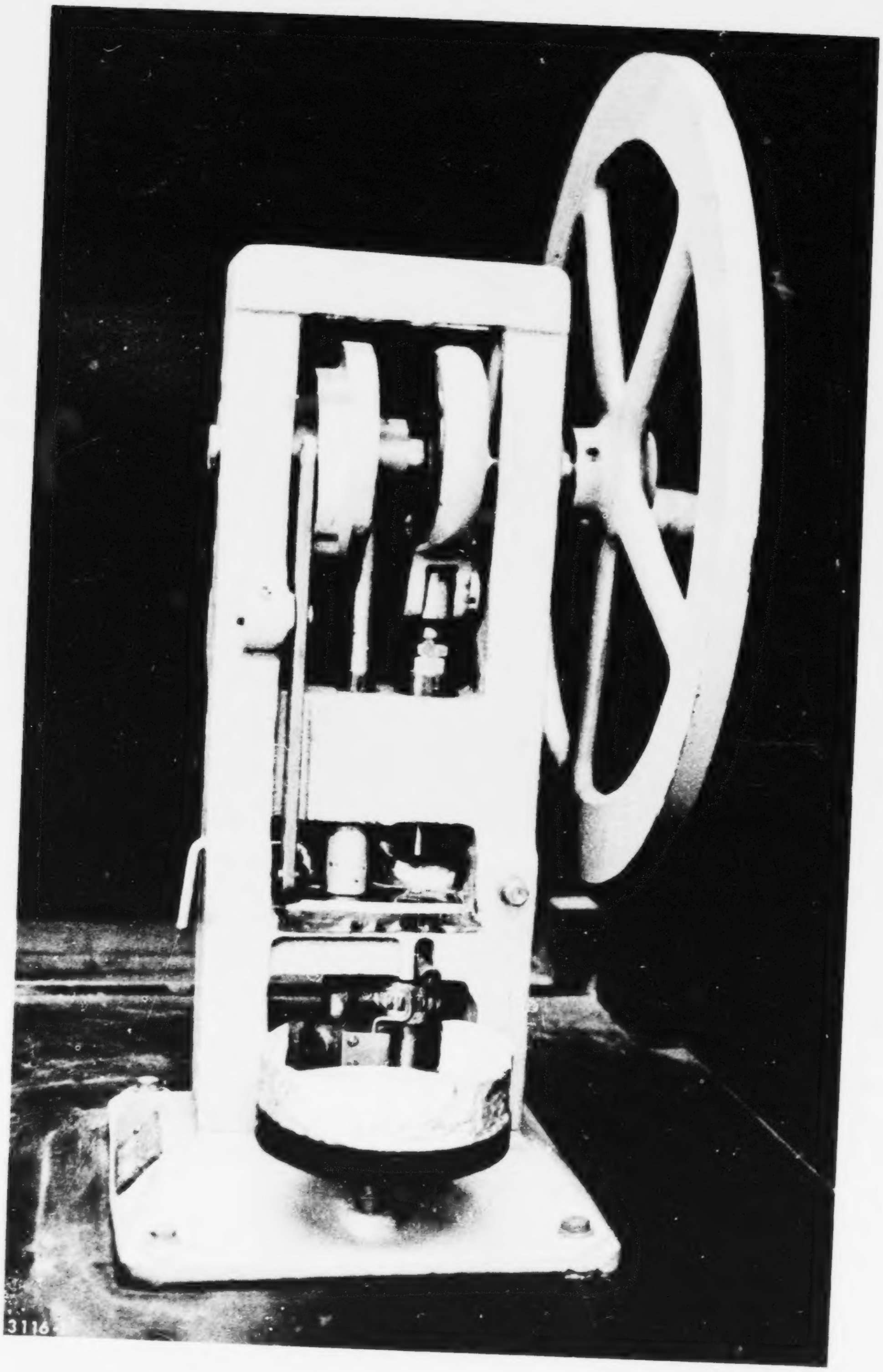


Figure 14. Catalyst Pelletizer

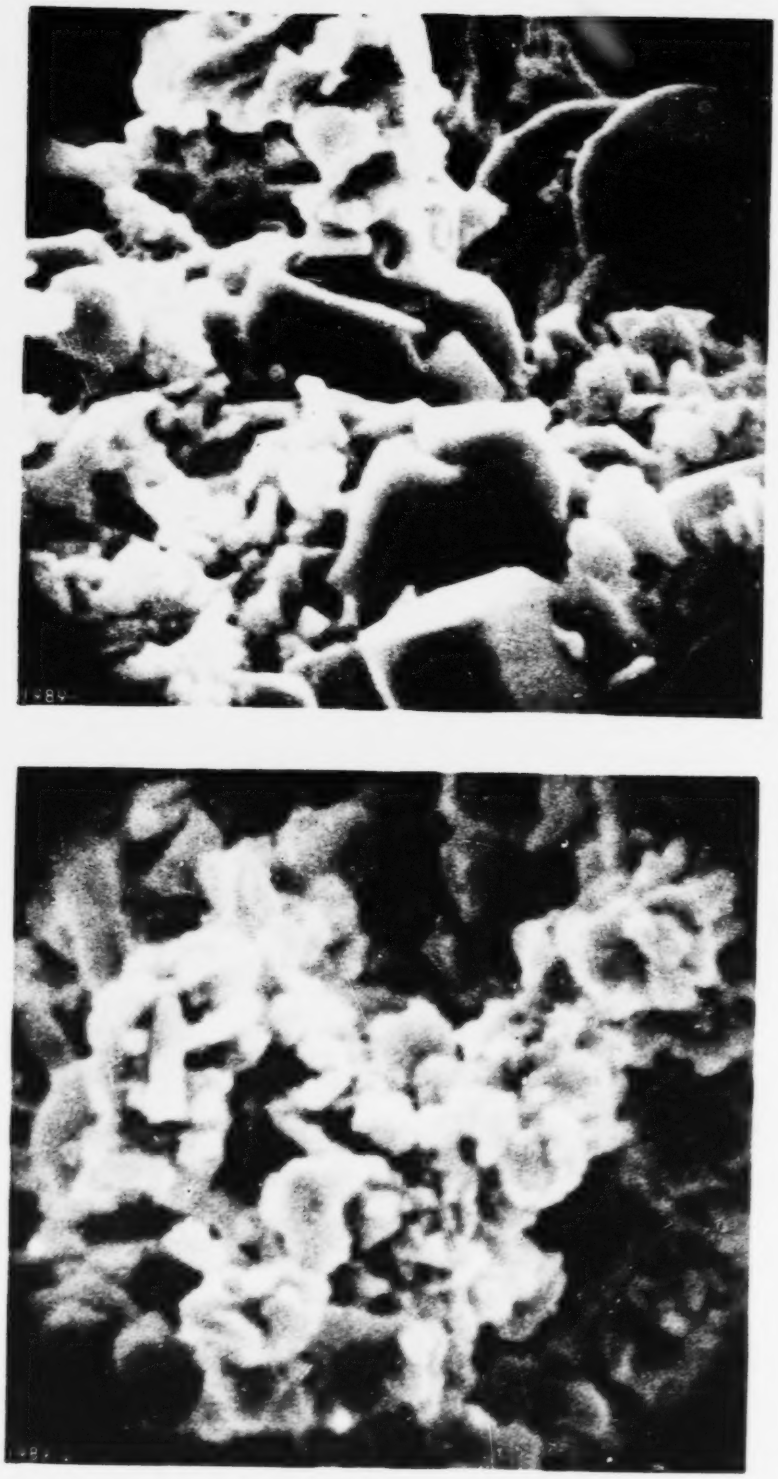


Figure 15. Catalyst Pellet Surface (6000X) Before (Upper) and After (Lower) Heating at 800°F

NOT REPRODUCIBLE

A second modification of preparation consisted of mixing catalyst and promoter, calcining, grinding the "clinker" and dry mixing with the support and pelletizing.

A third modification consisted of soaking the support in a solution, or suspension, of catalyst and promoter, and evaporating the solvent (water) to deposit the salts and oxide on the support.

III. CATALYST TESTING PROCEDURE

A complete test of a given catalyst would involve determining the conversion obtained by varying each of the following:

- Temperature
- Concentration of SO_2
- Concentration of O_2
- Contact Time
- Concentration of other constituents, active or inert

The rate of reaction is also dependent upon the catalyst surface area, pore volume and size as well as the variables listed above.

Testing of the effects and interactions of all the variables on conversion for a large number of catalysts would have required an inordinate amount of time and expenditure for the amount and usefulness of the information obtained. It was therefore decided to pursue a more rapid but less comprehensive test program for preliminary testing of catalysts.

Since the variation in SO_2 and O_2 concentrations in stack gas is not large and both are at low absolute concentration, average values of their concentrations were employed and kept relatively constant throughout the tests. Thus, a feed stream of 0.3% SO_2 and 3% O_2 would be representative.

Next, a standard set of test conditions was established as follows:

- Flow Rate - 40 cc/sec (space velocity 2000-2500 hr^{-1})
- "Standard" stack gas composition*
- Initial run temperature - 600°F

It was then necessary to select a common basis for evaluating different catalyst samples. A first approach considered "contact time" as the common base. It soon became evident that this was inadequate because the variation in bulk density, Table 1, among different catalysts, resulted in widely different amounts of catalyst showing the same contact time.

---

*Stack Gas Composition

	Vol.%
Nitrogen	82.15
Carbon Dioxide	14.70
Oxygen	2.80
Sulfur Dioxide	0.30
Nitrogen Oxides	0.05
	100.00

Table 1

CATALYST BULK DENSITY

Catalyst Code	Type	Weight (g)	Volume (cc)	Apparent Density (g/cc)
A	Vanadia	146.10	240	0.609
B	Pt	200.00	245	0.816
C	Vanadia	200.00	195	1.03
D-1	Vanadia	Sample Catalyst In Powder Form		
D-2	Vanadia	Sample Catalyst In Powder Form		
E	Vanadia	142.83	260	0.549
F	Pt	64.80	145	0.447
G	Pt/Fe	47.09	75	0.628

The second approach considered the W/F value, i.e., the weight of catalyst per mole of SO_2 per second. When results obtained using contact time as a basis were converted to a W/F basis, as in Table 2, they were found to fit reasonably well with the computer-predicted curves derived from rate equations in the literature as illustrated, for example, in Figure 16. This, then, provided a common basis for comparing different catalysts, namely: comparative conversion efficiency at the same temperature and W/F value. Further, the W/F value is related to space velocity (See Appendix V) thus permitting reasonably valid extrapolation from laboratory test data to process design.

In order to change the W/F value for a given weight of catalyst, it was only required to change the gas flow rate. Later, conversion isotherms are presented for some commercial catalysts at various W/F values attained in this manner.

In summary, the procedure employed for the comparative evaluation of experimental catalysts consisted of determining the conversion efficiency (% SO_2 converted) at the same W/F value under the standard test conditions enumerated above. In a number of instances, catalysts were studied more broadly, as with some of the commercial catalysts discussed below.

Table 2

CATALYST TEST DATA

	Catalyst	Weight of Catalyst, W (gms)	Flow, F (cc/sec)	W/F gm sec/cc	Temp. °F	Percent Conversion
1.	A (pellets)	5.8	40	0.145	800	38%
2.	A (pellets)	5.8	60	0.0966	800	29%
3.	A (pellets)	5.8	60	0.0966	650	3.5%
4.	A (pellets)	5.8	60	0.0966	900	46%
5.	A (pellets)	5.7	60	0.0950	900	25%
6.	A (crushed)	6.0	40	0.150	800	52%
7.	A (crushed)	6.0	40	0.150	850	68%
8.	A (crushed)	6.0	60	0.100	850	58%
9.	A (crushed)	6.0	60	0.100	650	3.5%
10.	A (crushed)	6.0	60	0.100	900	68%
11.	B	8.5	60	0.142	850	50%
12.	B	8.5	40	0.212	850	65%
13.	B	8.5	60	0.142	650	15-11%
14.	B	8.5	60	0.142	900	70%
15.	C	9.7	40	0.242	850	62%
16.	C	9.7	60	0.162	850	54%
17.	C	9.7	60	0.162	650	8-3%
18.	C	9.0	60	0.150	850	48%
19.	C	9.0	100	0.090	850	23%
20.	C	9.0	60	0.150	900	53%
21.	D-1	7.6	60	0.127	900	57%

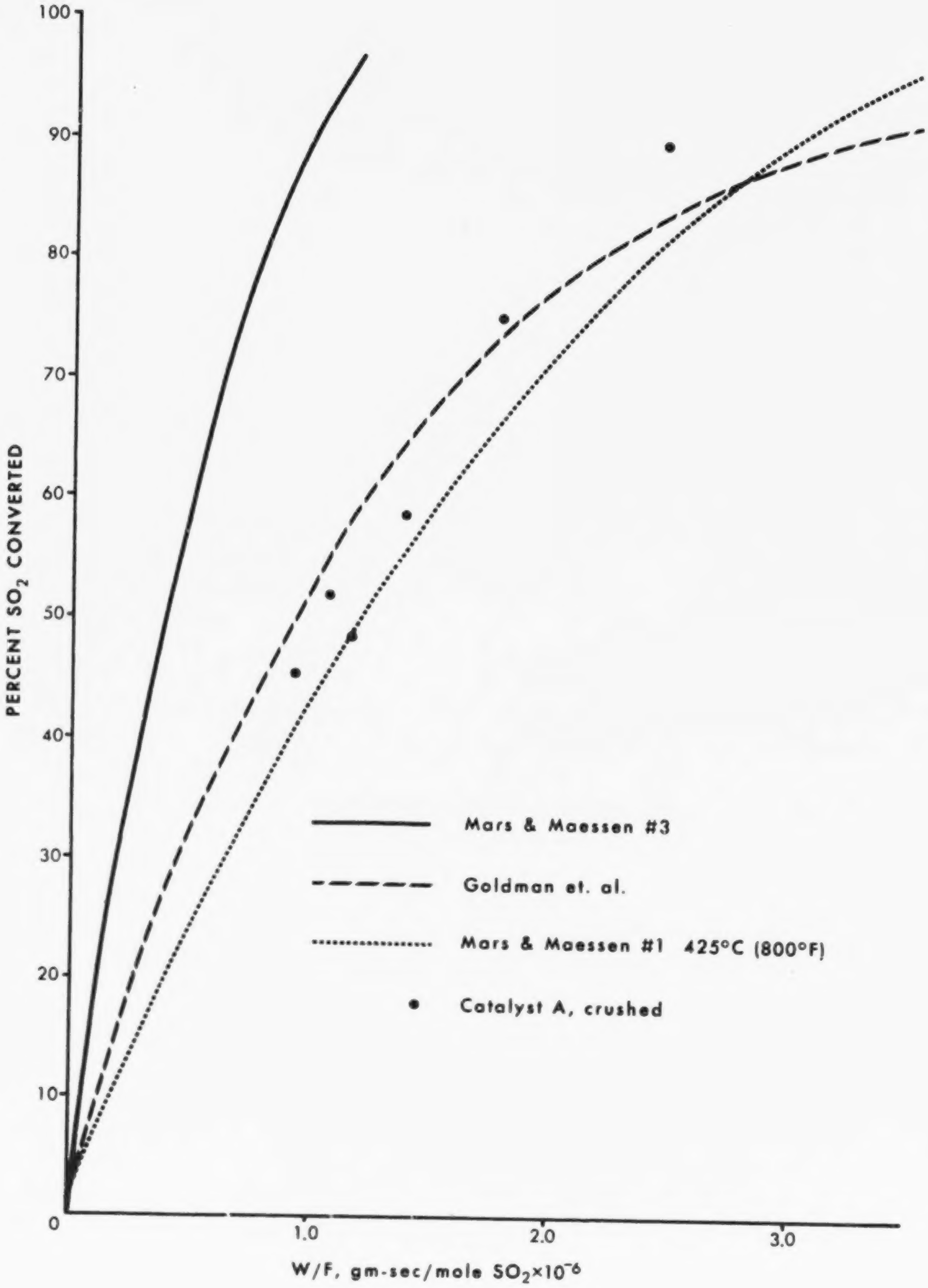


Figure 16. Comparison of Experimental and Predicted Effects of W/F on Conversion at 800°F

IV. CATALYST TEST RESULTS AND DISCUSSION

From statements found in the literature, there was reason to believe that commercially available SO_2 oxidation catalysts, designed for use in sulfuric acid plants, would be effective with flue gas. To support this belief, commercial vanadia catalyst samples were obtained from major U. S. producers. One platinum catalyst, commonly employed in hydrocarbon reforming, was also obtained.

A. Commercial Vanadia Catalysts

In the particular case of vanadia catalysts, conversion efficiency is rather poor below 790°F and above 930°F for a single pass converter system due to greatly reduced activity at the lower temperature and the rapid shift in equilibrium at the higher temperature. Consequently, three temperature levels were selected as representative of vanadium catalyst activity, namely: 800°, 850° and 900°F. By experimentally defining the W/F conversion profiles at these temperature levels, a rather complete picture of the relative merits of the various samples was obtained. With the addition of catalyst physical properties, it is possible to predict the weight of catalyst needed for 90+% conversion of a given SO_2 concentration at constant flow and temperature conditions.

Only two of the four commercial samples received were studied extensively. A few data points were obtained with the remaining two to support the assumption that they too would, in general, effect conversion of SO_2 under flue gas conditions.

Approximately 20 experimental runs were required to determine the W/F conversion profiles presented for the two vanadia catalysts. The conversion isotherms are shown in Figures 17 and 18. Examination of the curves indicates that 90% conversion of SO_2 to SO_3 may be attained at typical stack gas concentrations ($\sim$0.3%) providing the indicated temperature, flow, and catalyst charge requirements are met (See Appendix I for commercial catalyst test data).

As would be expected, there are point-to-point differences in the performance of any two different commercial catalysts, shown in Figures 19 through 21. This is not only true "between manufacturers" but also "within manufacturers". Nevertheless, the data support the conclusion that the commercially available vanadia catalysts are applicable, in a technical sense, to a process for removal of sulfur dioxide from flue gas. Furthermore, it is likely within the scope of the manufacturers' present technology to adjust the performance of these catalysts to give an incremental increase in efficiency under flue gas conditions. Process economics and competition will probably motivate such adjustment. Additional data relating to vanadia catalysts can be found in Appendix III, Volume I.

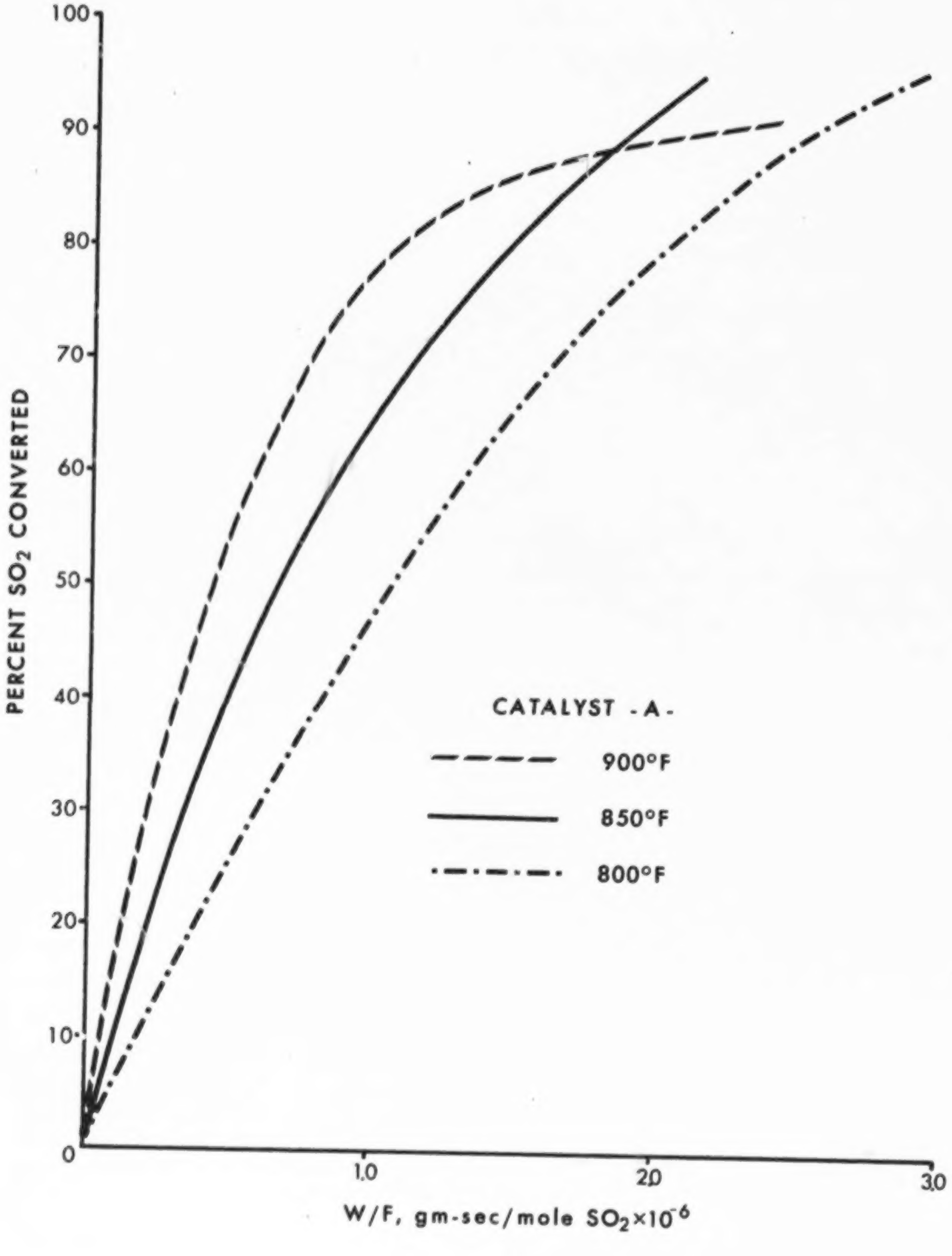


Figure 17. W/F-Conversion Profiles for Catalyst 'A'

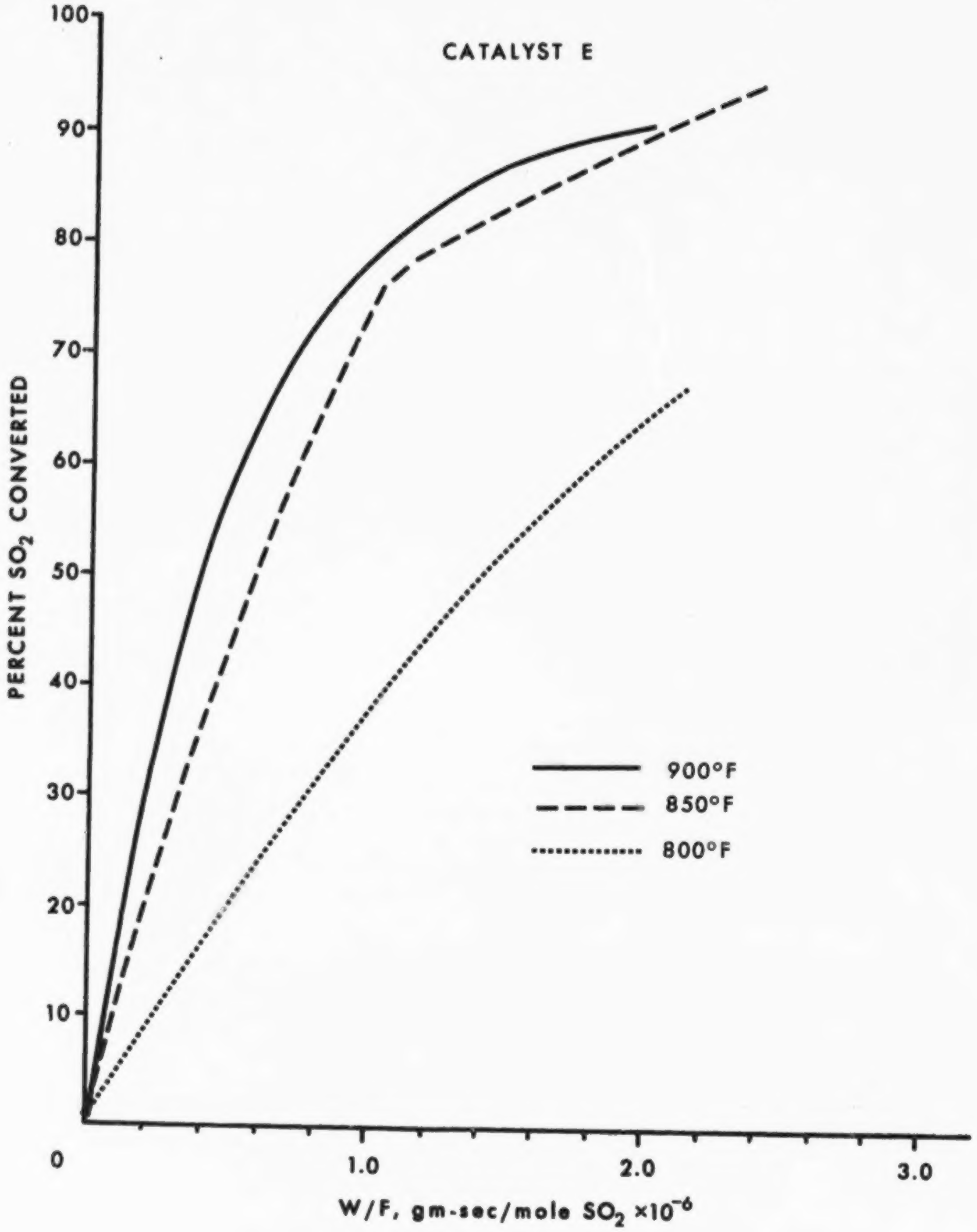


Figure 18. W/F-Conversion Profiles for Catalyst-E

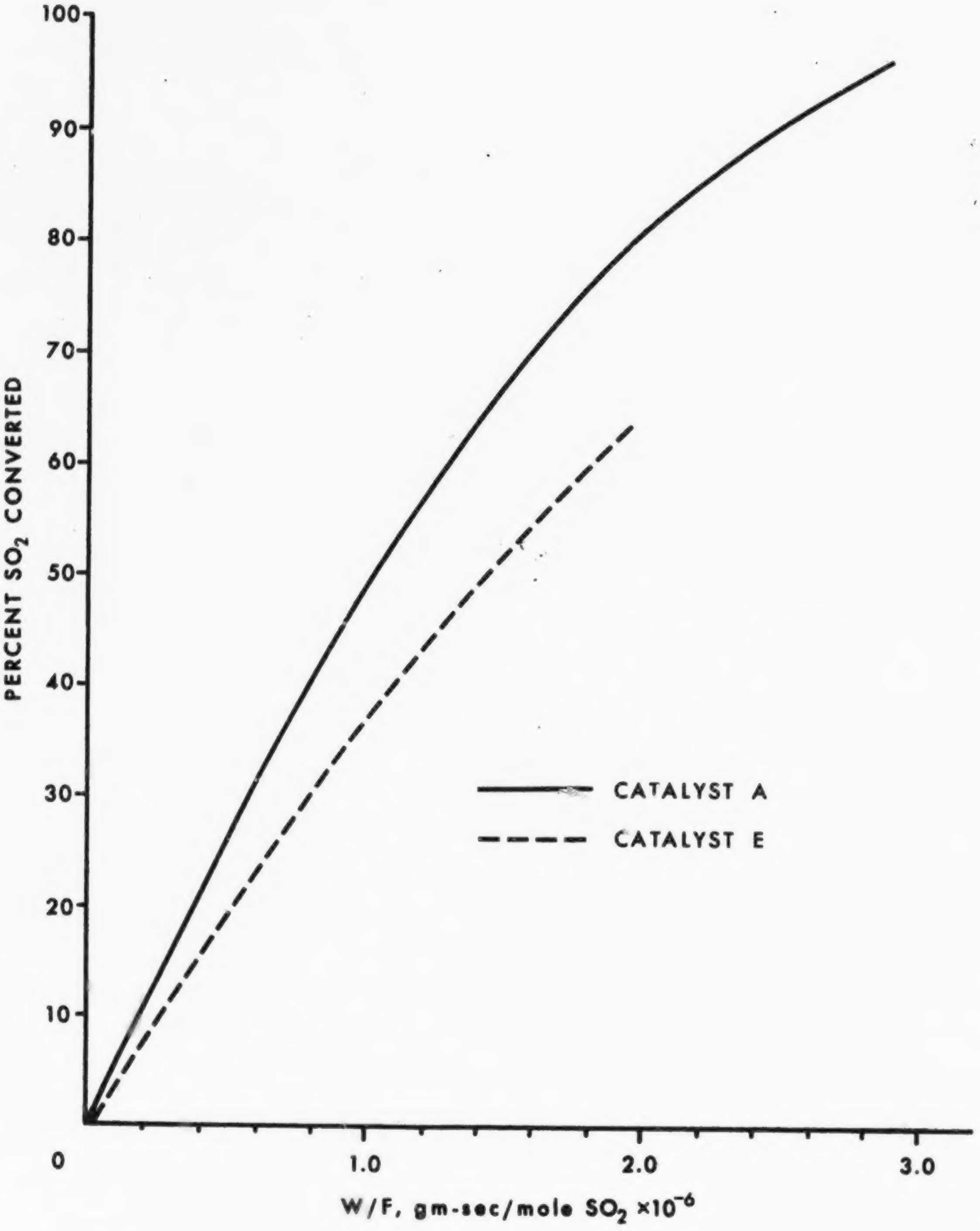


Figure 19. Comparative Conversion Efficiency of Two Commercial Vanadia Catalysts at 800°F

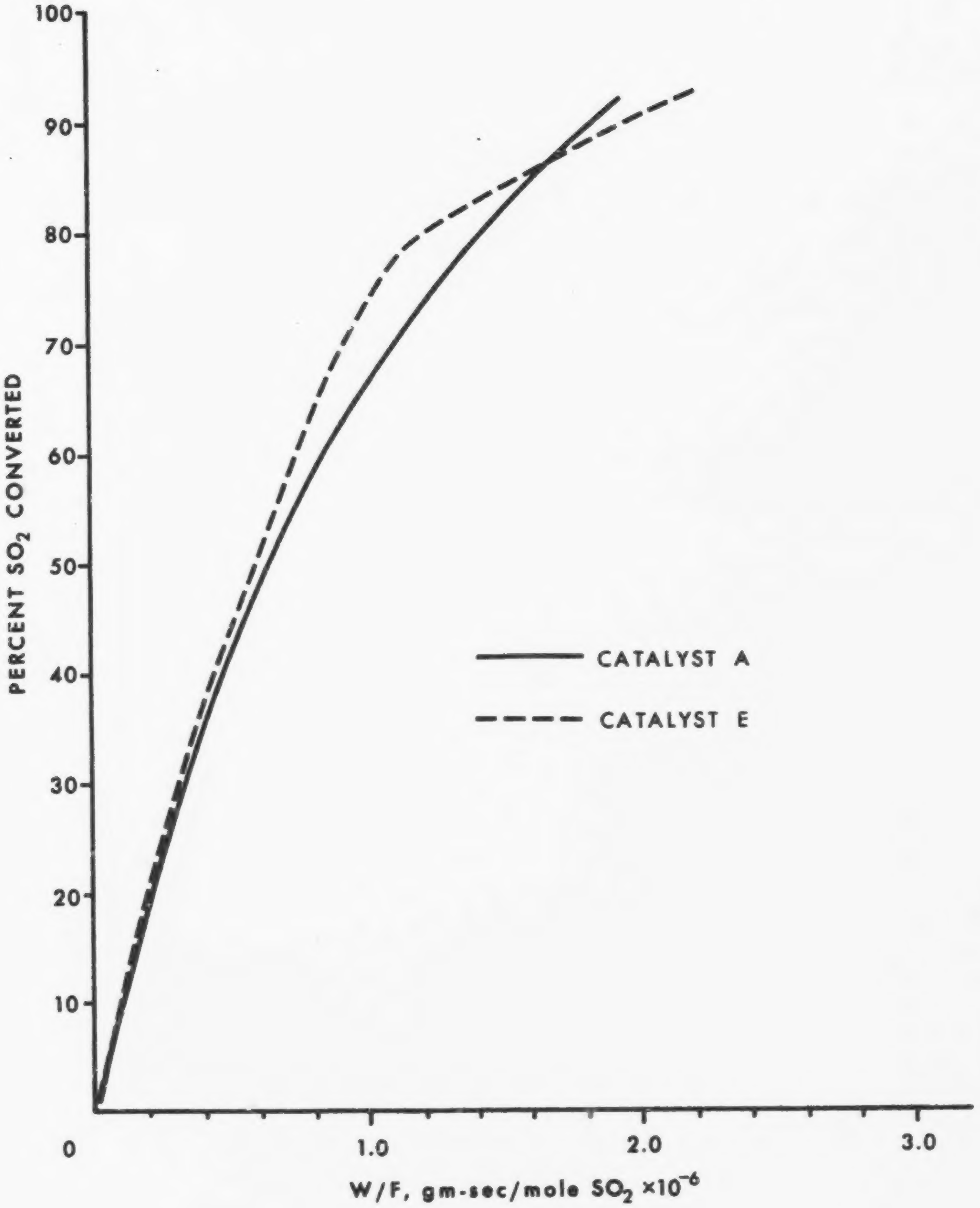


Figure 20. Comparative Conversion Efficiency of Two Commercial Vanadia Catalysts at 850°F

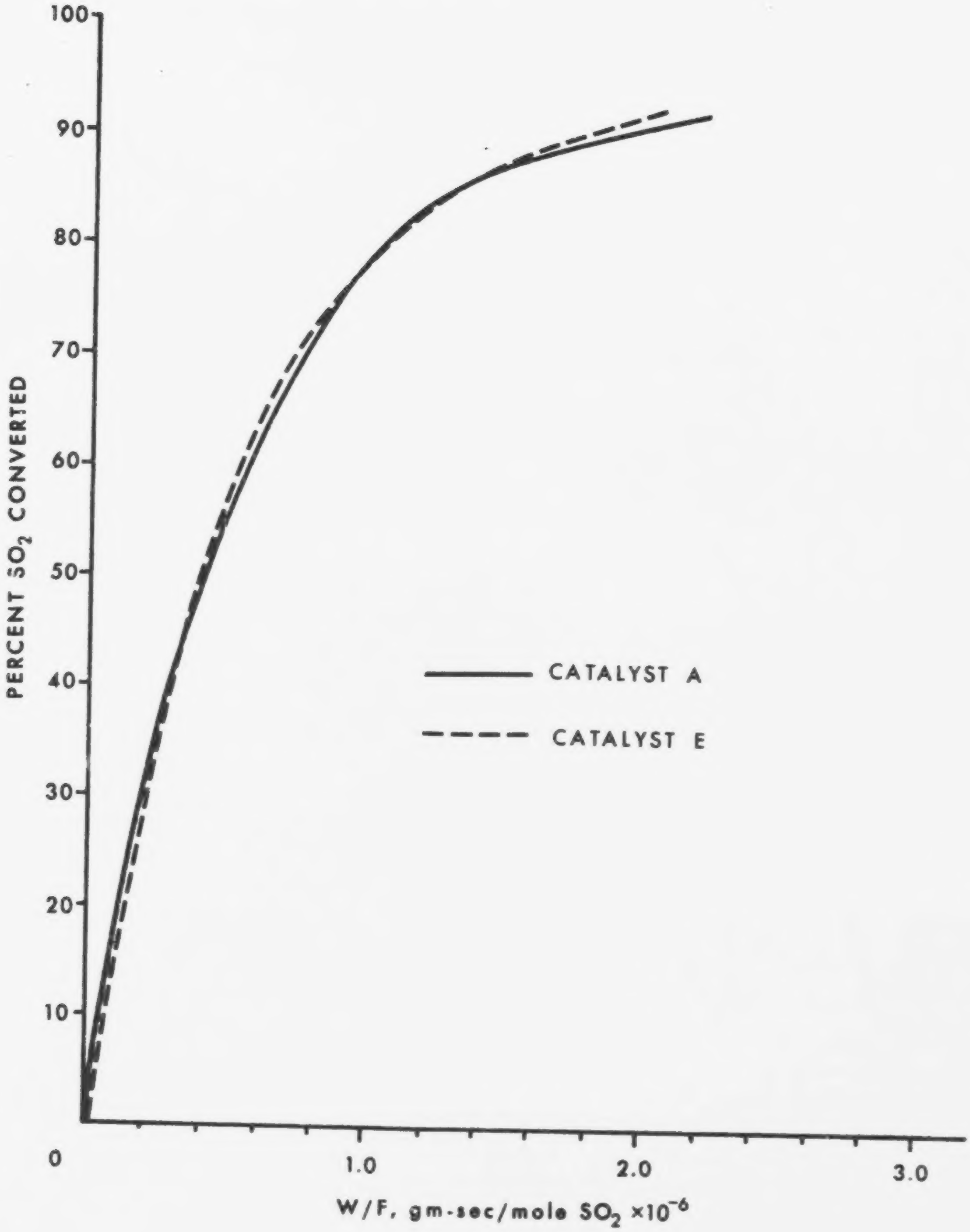


Figure 21. Comparative Conversion Efficiency of Two Commercial Vanadia Catalysts at 900°F

B. Commercial Platinum Catalyst

Platinum catalyst designed for contact sulfuric acid plants is no longer made commercially in this country. The platinum catalyst sample studied here was designed for hydrocarbon reforming. How much difference in composition or nature one might expect in catalysts designed for these seemingly different purposes is not known. However, as indicated by the conversion isotherms in Figure 22, this particular catalyst gave a creditable performance. Furthermore, a point-to-point comparison of the performance of the platinum and vanadia catalysts at flue gas conditions presents essentially the same pattern as that found in the literature for the comparative performances of the two types of catalyst at "standard" contact plant conditions. This can be seen in Figure 23 for comparative performance at 900°F.

In contrast to the vanadia catalyst, the platinum displayed an unstable equilibrium at constant reaction conditions for a considerable period of time at each set of conditions tested. The effect of time on the conversion efficiency is shown in Figures 24 and 25. Sometimes as long as six hours was required before a stable, reproducible conversion was obtained.

Although vanadia and platinum catalysts would seem to be about equivalent in performance, they are worlds apart in cost. A cost analysis of these two catalysts, summarized in Table 3, indicates that platinum must be at least ten times as effective as vanadia to be comparable in cost with the vanadia catalyst. Decline in platinum catalyst cost is not likely in the near future in view of the rising costs of labor and the metal itself (Details in Appendix VI).

C. Experimental Catalysts

Considering only the performance characteristics of vanadia and platinum catalysts, a major disadvantage with both, relative to a flue gas process, is their high reaction temperature. This generates both economic and engineering difficulties in practical application. Consequently, it seemed logical to seek a catalyst with an operating temperature nearer to that of the flue gas entering the stack, i.e., about 300°F. This temperature, however, is well below the dew point of the sulfuric acid produced through oxidation of the flue gas sulfur dioxide. Thus, a catalyst system operating at this temperature would soon be swamped with liquid sulfuric acid.

A corollary to the "low" temperature approach is identification of a catalyst which is more active throughout the present operating temperature range than are commercial vanadia catalysts. If a

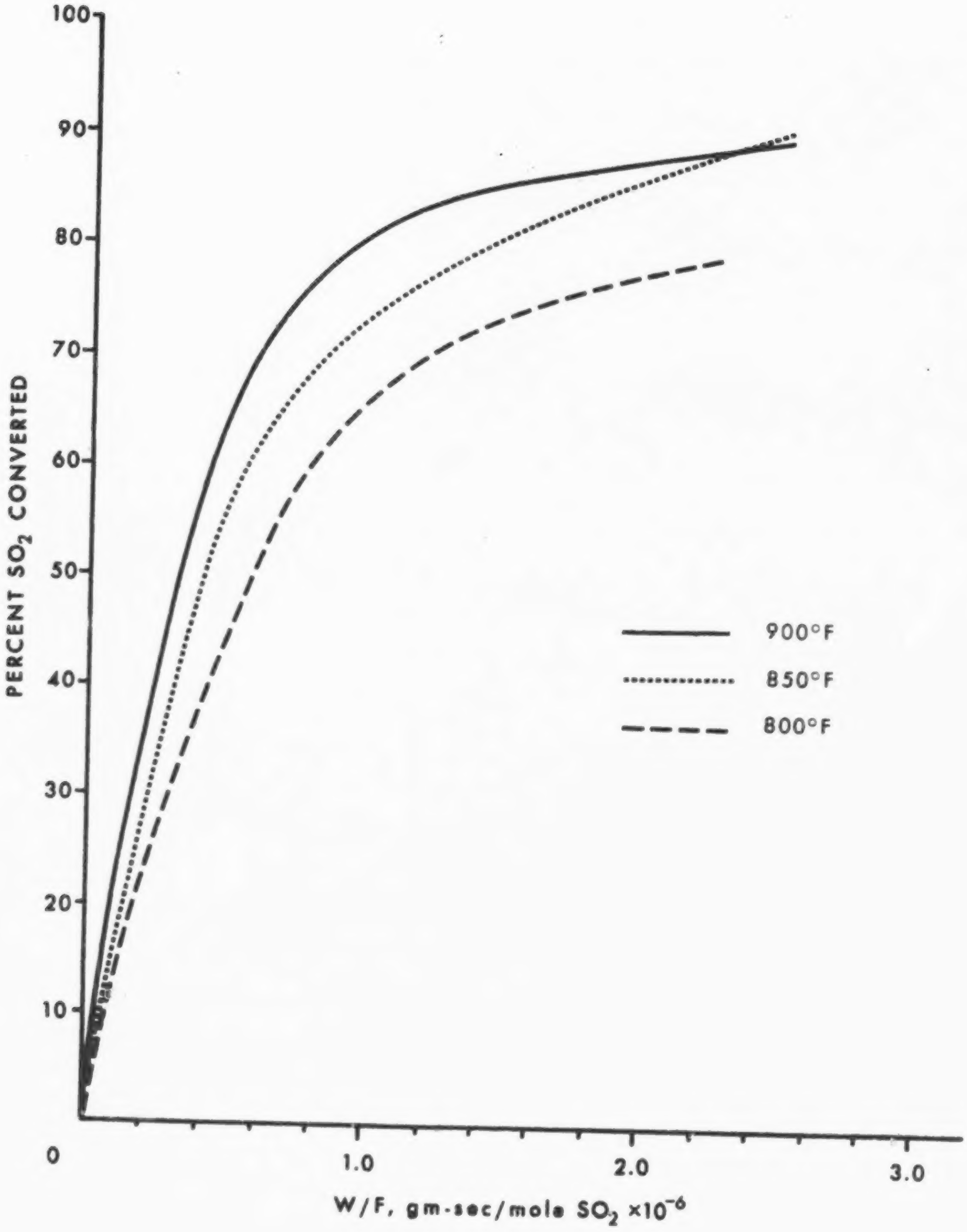


Figure 22. W/F-Conversion Profiles for Commercial Platinum Catalyst

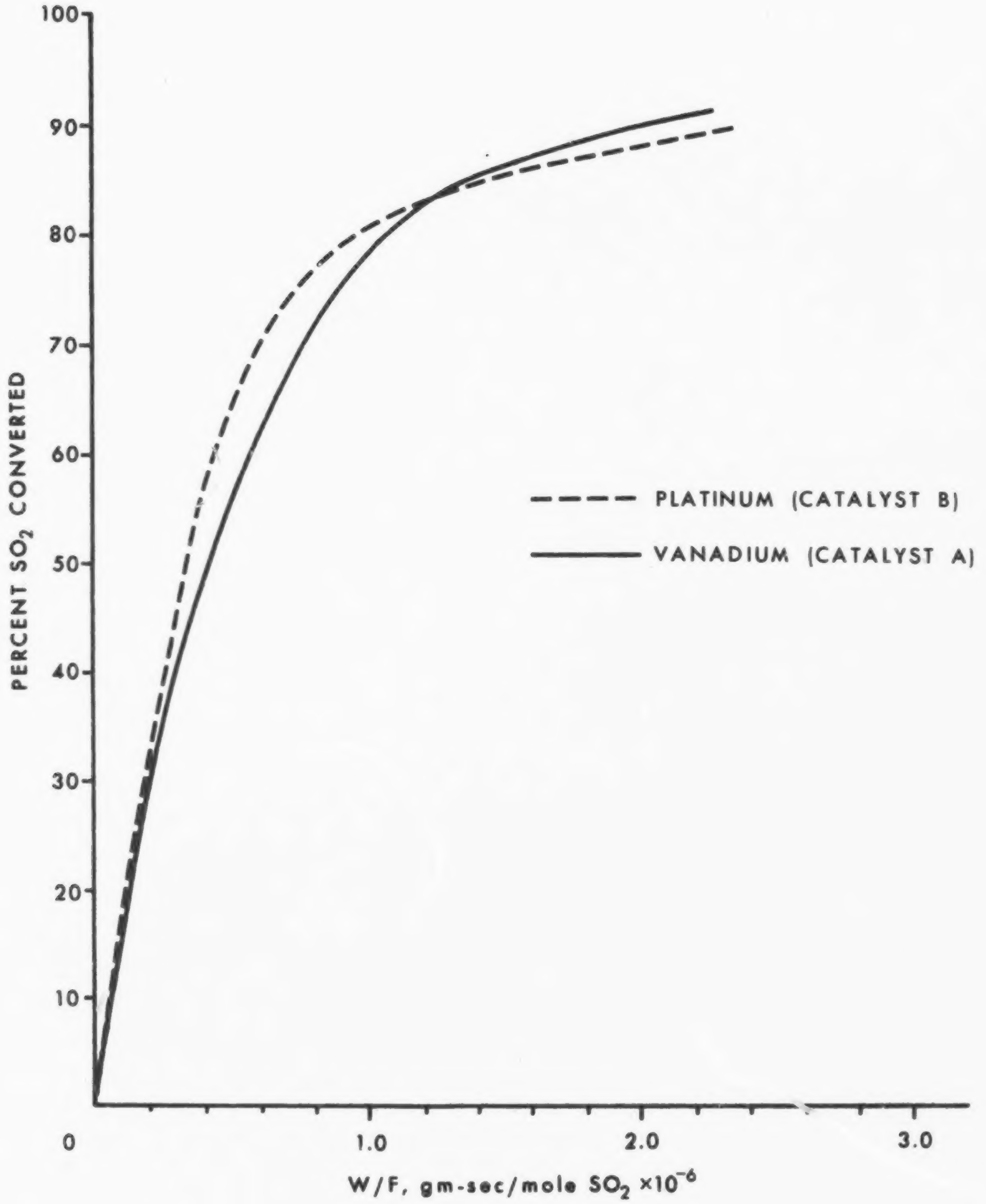


Figure 23. Comparative Conversion Efficiency of Platinum and Vanadia Catalysts at 900°F

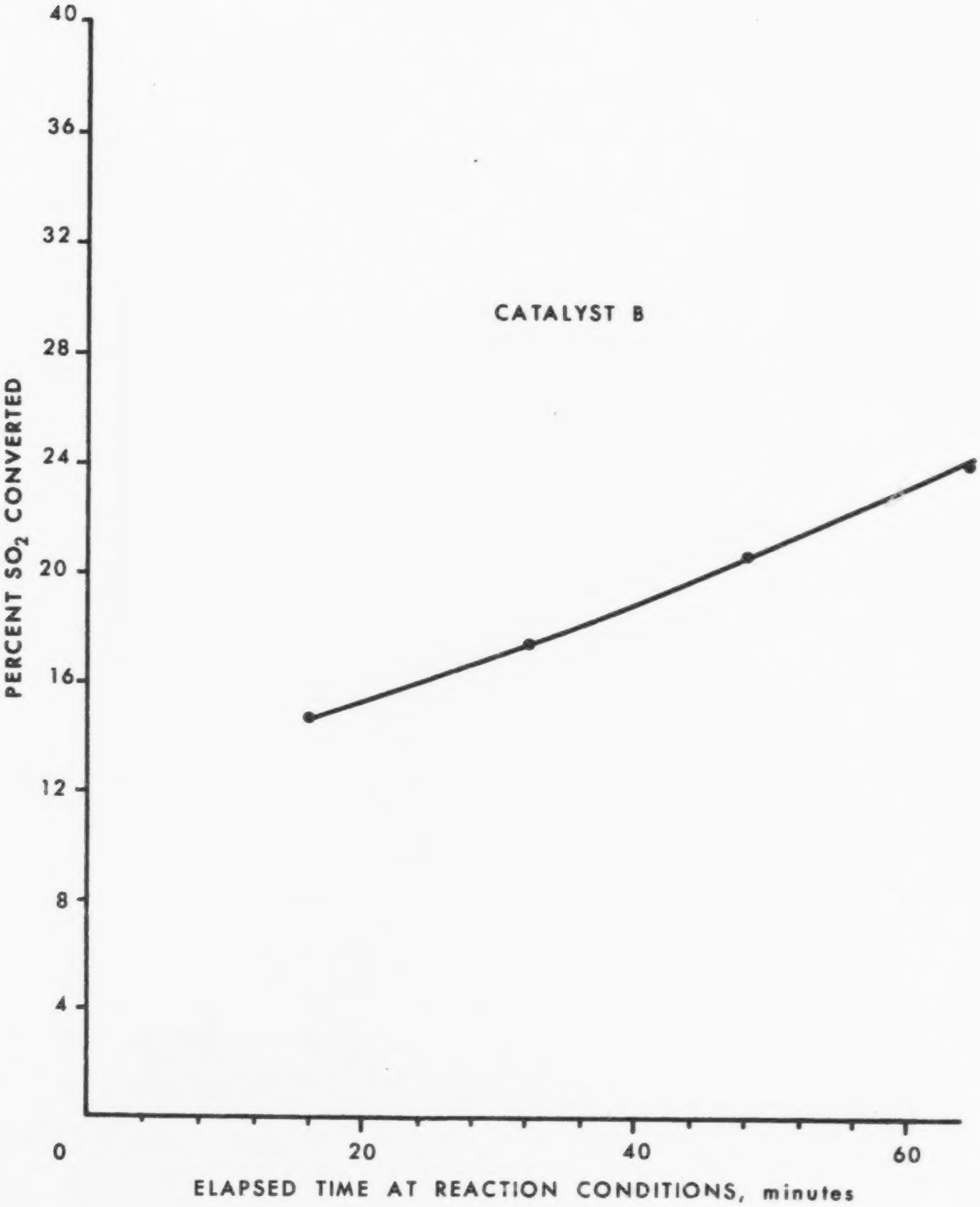


Figure 24. Effect of Time on Conversion Efficiency of Catalyst-B at 800°F, Constant Reactor Conditions (Run No. 6)

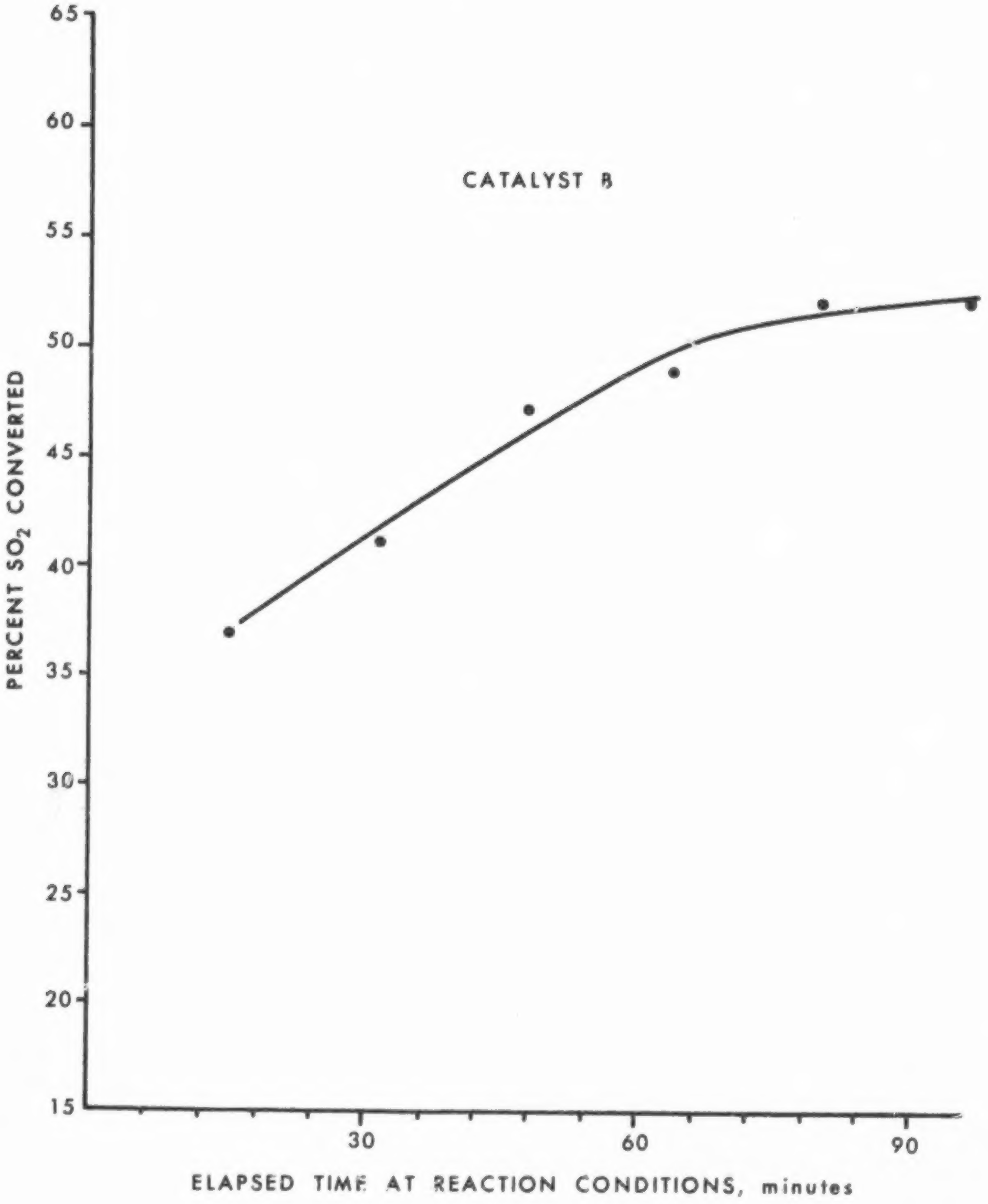


Figure 25. Effect of Time on Conversion Efficiency of Catalyst-B at 800°F, Constant Reactor Conditions (Run No. 7)

Table 3

SUMMARY OF ECONOMICS FOR VANADIA AND PLATINUM CATALYSTS(3)

	V Catalyst	Pt Catalyst
Volume, Cu ft(1)	30,300	3,020
Initial cost, dollars(2)	1,250,000	12,800,000
Regeneration cost, dollars(2)	---------	1,032,000
Capitalized cost, dollars(2)	3,920,000	20,380,000

NOTES: (1) Estimate of the volume of platinum catalyst that would be equal in cost to the estimated capitalized cost of vanadia catalyst for 90% conversion in flue gas.

(2) Estimates are based on the same W/F ratio for platinum and vanadia catalysts.

(3) Assumptions used for comparison of platinum and vanadia catalysts:

General:

a. rate of return: 8% per year

Vanadia Catalyst:

b. amount used for the oxidation of SO_2 in flue gas: 30,300 ft^3

c. price: \$41/ft^3

d. packed density: 36.8 lb/ft^3

e. catalyst life: 5 years

Platinum Catalyst:

f. catalyst contains 0.5% platinum

g. packed density: 50 lb/ft^3

h. catalyst cost: cost of platinum + \$2.75/lb catalyst, (for manufacturing cost)

i. regeneration cost: \$0.75/lb catalyst

j. regeneration interval: 2 years

k. loss of platinum during regeneration: 2%

l. price of platinum: \$110/oz (troy)

m. catalyst life: 30 years (including obsolescence and/or abandonment) catalyst were, say, 25-30% more effective than vanadia throughout the activity range, then at a temperature of 750°F, where vanadia shows only 60-70% efficiency, the new catalyst may yield a desirable 90% conversion efficiency.

Yet a third objective in testing experimental catalysts was to follow-up suggestions, or clues, in the literature that could lead to new catalytic compositions for efficient application to flue gas cleaning.

Observations made during the course of the commercial catalyst evaluation studies appeared to shed some light on the mechanism of vanadia catalysis as proposed in the literature:

$$SO_2 + 2V^{+5} + O^{-2} \rightleftarrows SO_3 + 2V^{+4} \qquad (1)$$

$$2V^{+4} + 1/2\ O_2 \rightleftarrows 2V^{+5} + O^{-2} \text{ (rate controlling)} \qquad (2)$$

$$VO_2,\ V_2O_5 \text{ (solid)} \longrightarrow VO_2,\ V_2O_5 \text{ (in solution in molten alkali pyrosulfates)} \qquad (3)$$

In our catalyst test unit, at the end of a run, the mixed gas stream is turned off and replaced by a stream of nitrogen at the same bed temperature. The nitrogen purges the system for roughly an hour at temperature; then the unit is shut down. This operation, supplanting the mixed gas stream with nitrogen, has the effect of "freezing" the equilibrium mixture in Equation (2). We compared pellets of a catalyst "frozen", in this manner, at 625°F and at 800°F by placing them separately in distilled water. The pellets representative of the lower temperature were bluish in color and produced a blue solution, characteristic of $V+^4$. Pellets representative of the higher temperature were brown, characteristic of $V+^5$ and imparted no color to the water. This qualitative observation appeared to confirm the belief that at the lower temperature, certainly the equilibrium mixture was predominantly $V+^4$, but it raised the question of whether Equation (2) is inherently temperature-dependent or whether it must act in molten solution, which condition is temperature-dependent. If it were solely the latter, then a possibility of defining a system of low melting promoters is offered.

There are salts which melt in the desired "low" temperature range, and using some of these, fleeting evidence supporting the rationale above was observed. The short life of activity in the lower temperature region is attributed to instability of the salt either at temperature or in the presence of SO_3.

Again we have seen vagrant activity of this type when, for instance, residual chlorine in platinum catalyst is replaced with thiocyanate. The increased activity of the platinum was short-lived because, it is proposed, of the reaction of sulfuric acid produced with the thiocyanate to release thiocyanic acid.

Many catalyst compositions were prepared and tested in the search for a stable low temperature, or more active high temperature catalyst. Included also were a number of experimental catalysts from various vendors around the country. These data are quite extensive and, for that reason, are tabulated in Appendix II. All catalyst compositions beginning with the code letter (M) are compositions prepared in our laboratory. Other codes represent experimental samples received from industrial catalyst vendors. The latter were not accompanied by details of their compositions, as this information is considered proprietary by the vendors.

It is interesting to note, throughout Appendix II, several compositions (designated by stars) which exhibit extremely low temperature activity. The apparent conversion efficiency reported, while accurate, may be somewhat deceiving, as these data may not represent optimum operating conditions of the catalyst. However, the data does indicate the possibility that these compounds have potential as stoichiometric removal systems similar to the limestone injection process. As mentioned previously, their performance may be affected by several parameters not yet defined.

It is felt, that the behavior nearly always observed, i.e., fleeting low temperature activity, can be explained on the basis of the product SO_3 reacting with the metal oxide catalyst forming sulfate, or with the promoter, as with $KHSO_4$:

$$2\ KHSO_4 + SO_3 \longrightarrow K_2S_2O_7 + H_2SO_4$$

As the bisulfate is converted to pyrosulfate, the melting point of the salt rises, with a corresponding decrease in activity at the lower temperature of the test.

These observations are interesting in that they seem to support our approach to a low temperature catalyst. But, they also illustrate the necessity of stability of the promoter system in the presence of SO_3. No material tested showed greater activity or stability than vanadia under test conditions.

In the light of these cumulative observations, it is possible to prescribe the requirements for a "low" temperature vanadia catalyst, which, in the end, resolve to the requirements for the promoter salt.

These requirements are:

a. Salt (or salt system) should be completely molten and non-volatile in the 450°-500°F range.

b. Vanadia must dissolve in molten salt and, probably, must ionize.

c. Salt (or system) must be chemically stable in temperature range.

d. Salt (or system) must be chemically stable in the presence of O_2, SO_2 and SO_3.

These requirements assume that sorption and desorption of reactants and products are not limiting, which is the current assumption for commercial vanadia catalysts.

D. Molecular Sieve Adsorption Studies

Molecular sieves had been shown in the literature to be useful in many applications as heterogeneous catalysts and as vehicles in studies of catalysts and catalyst mechanisms. However, we could find no publication which revealed specific studies to determine their merit as support material for SO_2 oxidation catalysts. As the monodisperse nature of the zeolite pores and their extremely high specific area were characteristics favorable for maximum contact conditions between the SO_2 and active catalyst sites, samples were obtained and used as support material for two previously tested compositions. No alteration of the catalyst characteristics was seen.

Zeolite materials are also well known for their adsorption characteristics with regard to the various constituents in stack gas, and we wished to know if these characteristics would be an aid or hinderance in their use as a support material. Adsorption efficiency profiles at four temperature levels between ambient and 250°F were established for (4) different molecular sieve materials. These data are shown in Appendix VII. As regards materials SK-410 and SK-400, both of which showed relatively high SO_2 adsorption efficiency, the effects of a 30% reduction in adsorption bed contact time are also shown.

E. SO_2 Removal Characteristics of "Red Mud"

During the course of our experimental catalyst testing program we were requested by NAPCA to perform evaluations of a material commonly termed "red mud," which we were informed is a waste by-product of aluminum ore processing operations, for its potential as a removal material for SO_2 in power plant stack gas.

Using the one sample sent to us, we ran a bed of the material through our catalyst testing system and obtained conversion efficiency vs. time profile as shown in Figure 26. In a further attempt to determine the constituents influencing the activity of red mud in the presence of SO_2, a mass spectrometer analysis was performed on a sample of exhaust gas from the reactor during the time period shown in Figure 26. No evidence of SO_3 was found. However, these results are inconclusive, as we were unable to determine the sensitivity of the instrument to small concentrations of SO_3.

Further tests were performed on the partially spent bed of red mud which produced the decay profile illustrated in Figure 26. Emission analysis of the sample revealed the presence of the following:

Fe -- Low Major
Si -- Low Major
Al -- Low Major
Ca -- Low Major ($\sim$10%)
Na -- 5 to 10%
Ti -- 5 to 10%
Zr -- 0.3%
Cr -- 0.1%
V -- 0.07%
Mg -- 0.03%
Mn -- 0.03%

Subsequently, duplicate fusions were performed on the spent sample to determine total sulfur content. Results were 5.38 and 5.34% sulfur. A water and acid insoluble residue resulted when the fusion was taken up in water. The best probability is that the residue was a titanium containing material.

According to stepwise numerical integration of the absorption versus time profile (Figure 26) the sample of red mud absorbed 288 cc SO_2 over a 95 minute contact time. The density of SO_2 at metering conditions is 2.6813 g/l. Accordingly, the sample absorbed 0.772 gm SO_2. Of this, 50% of the total would be sulfur, or 0.386 gms. The sample weighed 9.82 gms, and of this an average 5.36% was determined as sulfur, or 0.526 gms. Consequently, 0.140 gms of sulfur were unaccounted for.

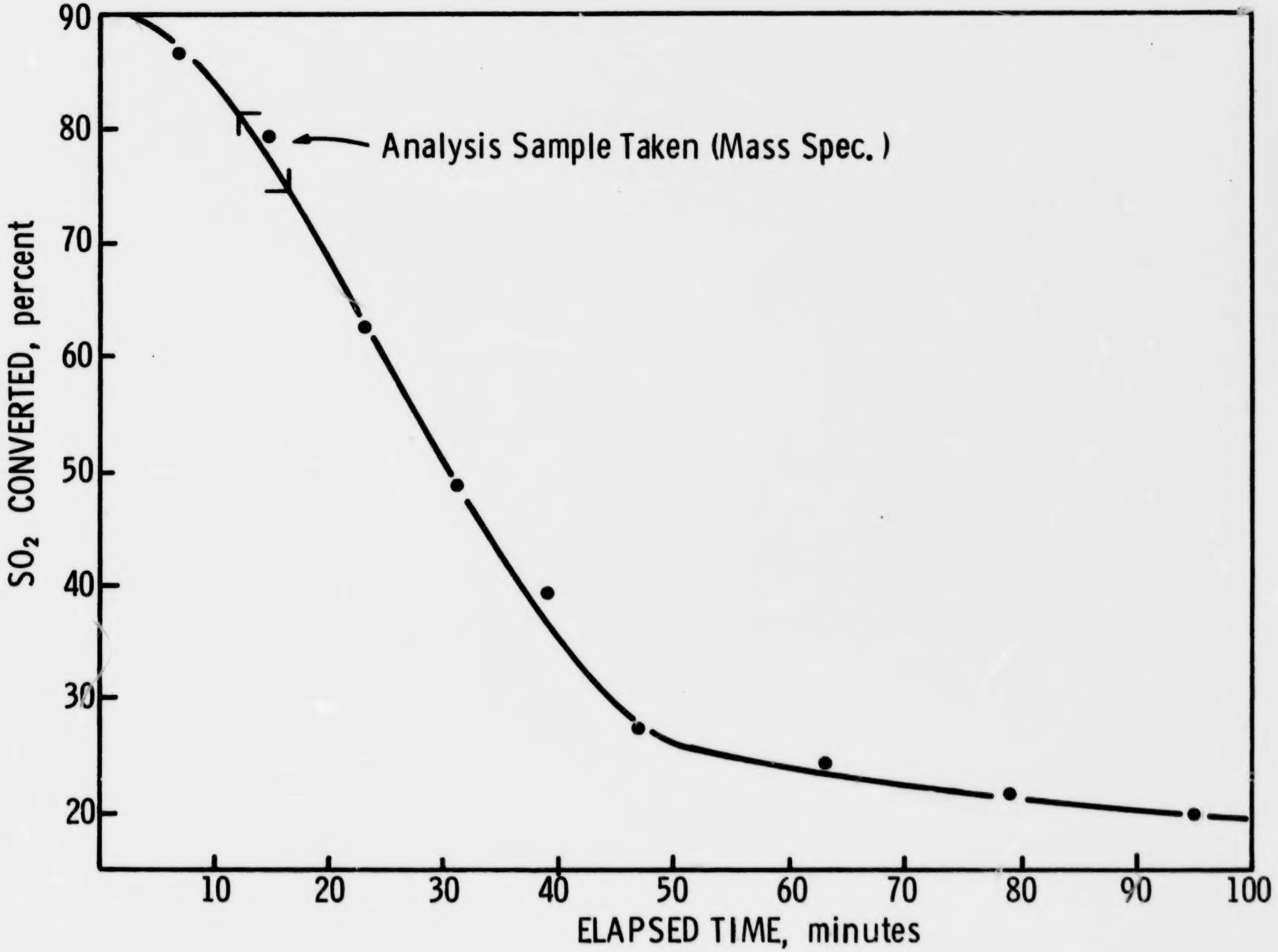


Figure 26. Conversion Efficiency versus Time Profile @ Constant Operating Conditions for "Red Mud"

Duplicate fusions were performed on a fresh sample of red mud with a result of 0.72% sulfur, or 0.071 gms sulfur in the sample initially. Thus, half of the missing sulfur was accounted for. This left about 13% of the total sulfur unaccounted for. However, this is within the accuracy of the overall technique.

These results indicate that the activity of the red mud is due to reaction between the SO_2 and various constituents of the sample, with subsequent formation of stable inactive sulfur compounds within the sample, causing the decrease in "apparent conversion" noted in Figure 26.

V. DEVELOPMENT OF A SIMULTANEOUS SO_x-NO_x REMOVAL PROCESS

It has long been recognized that high temperature combustion processes, including electric power plants, produce oxides of nitrogen. It was therefore a logical and desirable extension of our experimental program to check the effect various commercial catalysts had on existing NO_x concentrations in a power plant stack gas environment. In addition, we felt that a process which would simultaneously remove both SO_x and NO_x would have a decided advantage over a process removing only one of the pollutants.

Examination of the well-known technology of the Chamber Sulfuric Acid process indicated that nitric oxides could be scrubbed from their carrier gas by 60° Be sulfuric acid - successful removal being dependent upon the maintenance of equimolar concentrations of NO and NO_2. The resulting absorption of $NO + NO_2$ into sulfuric acid then produces nitrosylsulfuric acid ($NOHSO_4$), this formation resulting from the following reactions:

- $NO + NO_2 + 2H_2SO_4 \longrightarrow 2NOHSO_4 + H_2O$ (1)
- $2NO_2 + SO_2 + H_2SO_4 \longrightarrow 2NOHSO_4$ (2)
- $2NO_2 + H_2SO_4 \longrightarrow NOHSO_4 + HNO_3$ (3)

The nitric acid which accompanies the formation of $NOHSO_4$ in equation (3) is then soluble in the large excess of sulfuric acid.

A. Initial Laboratory Investigations

Realizing that a similar chemically favorable environment could be produced in the exhaust stream from our catalytic reactor, a small glass scrubber was constructed and installed downstream of the reactor as represented in Figure 27. Sufficient NO_2 was then added to the flue gas to meet the following minimum requirements:

- 2 mols NO_2/mole unreacted SO_2 in flue gas
- 1 mole NO_2/mole NO in flue gas

As we had no means available at this time to meter the amount of NO_2 into the system, an obvious excess was used (as evidenced by the characteristic color of NO_2 in the combined gas streams). The rationale here was that the excess NO_2 would react according to equation (3).

As soon as NO_2 was added to the reactor effluent, white crystals formed on the walls of the glass arm entering the bottom of the scrubber. The accumulation of these crystals shortly plugged the

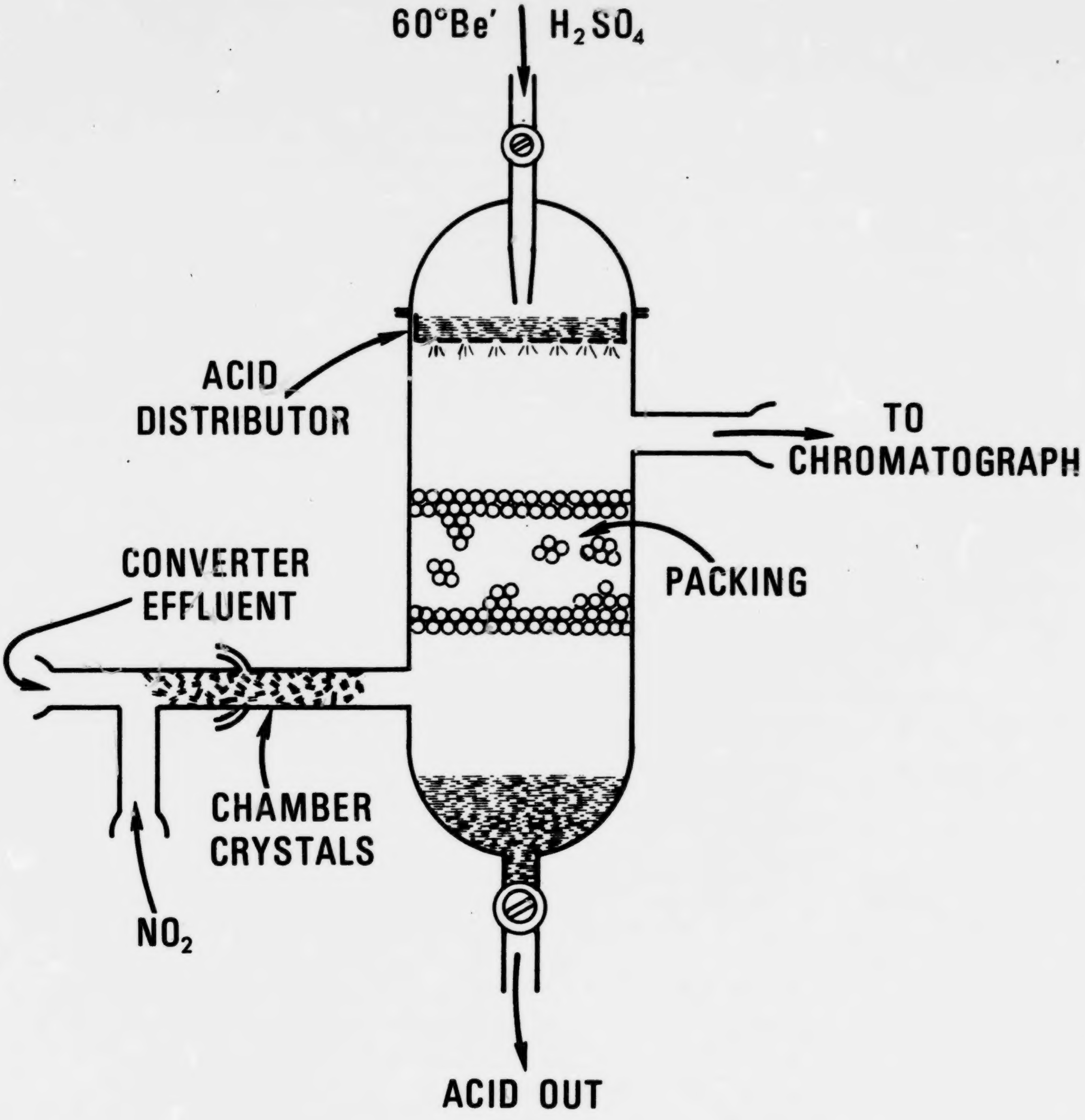

60°Be'
H_2SO_4
ACID DISTRIBUTOR
TO CHROMATOGRAPH
PACKING
CONVERTER EFFLUENT
CHAMBER CRYSTALS
NO_2
ACID OUT

Figure 27. Laboratory Arrangement for NO_x Scrubber

line. These crystals were qualitatively identified as "chamber crystals" or the anhydride of nitrosylsulfuric acid. This was not surprising, as the gas mixtures were dry. More interesting, however, was the reduction of unreacted SO_2 in the flue gas. At the time, the catalytic converter was effecting about 90% SO_2 conversion, but the exhaust from the scrubber showed 95+% conversion.

The NO_2 feed point was moved to the scrubber and the experiment repeated with no apparent formation of chamber crystals. The exhaust from the scrubber was then analyzed to determine the effect of NO_2 on the total conversion of sulfur dioxide. These data are shown in Table 4.

Table 4

EFFECT OF NO_2 ON TOTAL CONVERSION OF SULFUR DIOXIDE

Momentary total conversion without NO_2 addition to scrubber		89.1%
Momentary total conversion with NO_2 addition to scrubber	1)	94.9%
	2)	100.0%
	3)	99.2%
	4)	99.2%

Resulting product acid was shown qualitatively to contain nitrosylsulfuric acid.

The surprisingly high total conversion of SO_2 resulting from the use of NO_2 in the scrubber prompted further experiments. The flue gas was fed directly into the scrubber, by-passing the catalytic converter. Results of this experiment and a comparison with and without the use of the converter are given below.

Flow Scheme	% SO_2 Conversion
• Source → Converter → Scrubber	89.1
• Source → Converter → Add NO_2 → Scrubber	99.5
• Source → Add NO_2 → Scrubber	99.7

B. Vapor Pressure Studies on the System: $H_2SO_4-H_2O-N_2O_3$

Our success in obtaining almost 100% SO_2 oxidation by addition of NO_2 prompted the decision to design a process based on "modified" Chamber technology. Initial attempts to design such a process pointed out the need for vapor pressure data on the system: $H_2SO_4-H_2O-N_2O_3$. A literature search revealed two articles on the subject - one by Berl (Ref. 1) in 1934 and another by Tseitlin and Yavorskii (Ref. 2). Berl's data covered the range of sulfuric acid concentrations from 64.0% to 80.0%, at temperatures from 30°C to 150°C and for N_2O_3 concentrations from 0 to about 1%. The data of Tseitlin and Yavorskii covered an acid concentration range from 81.2% to 84.14% for corresponding N_2O_3 concentrations from 4.8% to about 10.0% at 50°C, 70°C, and 90°C.

A brief vapor pressure study was also initiated to check the data of these authors and to extend their work over the acid concentration range of 64 to 84%.

A pictorial representation of the experimental apparatus is given in Figure 28, which, incidentally, is quite similar to Berl's as given in Appendix 9. A 100-ml round-bottom flask was filled approximately half-way with the desired $H_2SO_4-N_2O_3$ mixture. The flask contained a teflon coated magnetic stirring bar. The flask was immersed in an oil bath with temperature maintained by an electric heater. A (-10° to 200°C) thermometer was suspended in the bath for temperature measurement. The flask was connected to one of two Hg manometers by means of rubber and glass tubing - the choice of manometer depending upon the expected vapor pressure. A MacLeod gauge was used to measure pressures from about 0.01 mm Hg to 5 mm Hg, and a U-tube manometer for pressures between 3-700 mm Hg. The system was connected to a vacuum source equipped with a liquid nitrogen trap and a dry ice trap which could pull a vacuum down to 0.007 mm Hg. There were two pinch clamps on the rubber tubing - one of which was immediately above the round bottom flask, and a second on the line to the vacuum source.

Our initial experimental results indicated that the data of these authors was low by a factor of about 3. However, we found that our procedure used to determine the vapor pressure was faulty. When this fault was corrected, the data agree satisfactorily with the data of Berl and Tseitlin and Yavorskii.

A description of the apparatus and procedure used to obtain the vapor pressure data is given in Appendix 8 to point out the faulty procedure and thereby prevent its recurrence in the future. The data is not included because it is of rather poor quality compared to that of Berl, Tseitlin, and Yavorskii, and would only serve to

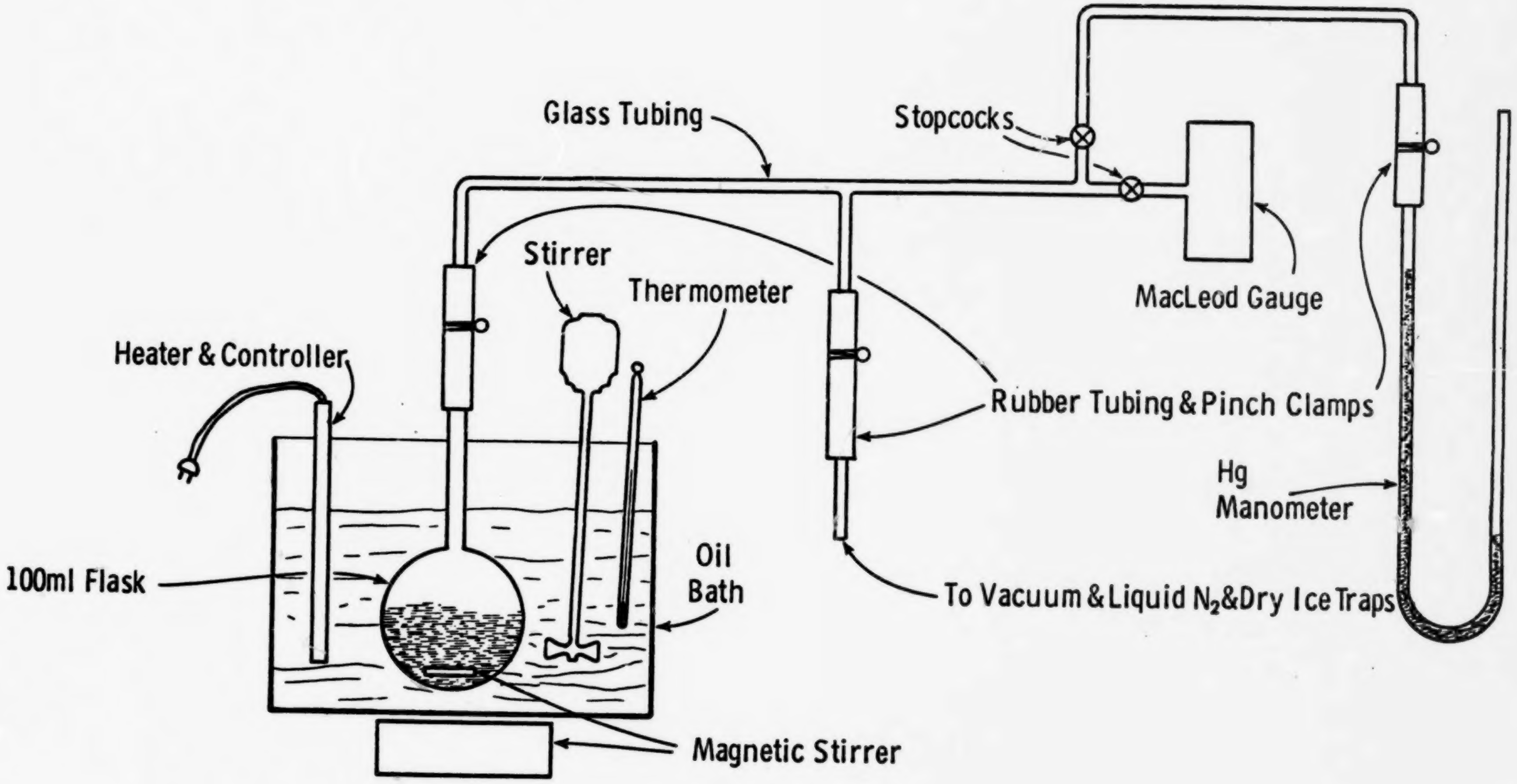

Glass Tubing
Stopcocks
Stirrer
Thermometer
MacLeod Gauge
Heater & Controller
Rubber Tubing & Pinch Clamps
Hg Manometer
100ml Flask
Oil Bath
To Vacuum & Liquid N_2 & Dry Ice Traps
Magnetic Stirrer

Figure 28. Experimental Apparatus for Vapor Pressure Studies

confuse the picture. Instead, a summary of their data is given in Figure 29. Berl's data was plotted on a log P(NO and NO_2) vs 1/T plot for 1.0% N_2O_3 mixture, and was limited to the following acid concentrations: 64.0%, 67.0%, 68.5%, 70.0%, 73.3%, 75.65%, 78.0%, and 80.0%. The best line was drawn through each of the acid concentrations. As the lines appeared to intersect near a single point, the "best point" was chosen and all lines were drawn to intersect at that point. The lines at 71 and 72% were included for convenience. Lines above 80% were obtained by extrapolating Tseitlin's and Yavorskii's data back to 1% N_2O_3 and forcing the line to pass through the intersection point. The greatest deviation from experimental data appears to occur at about 80%; however, these deviations differed in direction for the two authors. Berl's data shows somewhat lower NO and NO_2 vapor pressures (at 110°C and up) than that shown on the plot, whereas Tseitlin's and Yavorskii's data show somewhat higher NO and NO_2 pressures at 80%.

The vapor pressure data given in Figure 29 can be extended to other N_2O_3 concentrations by multiplying by the N_2O_3 concentration in wt%.

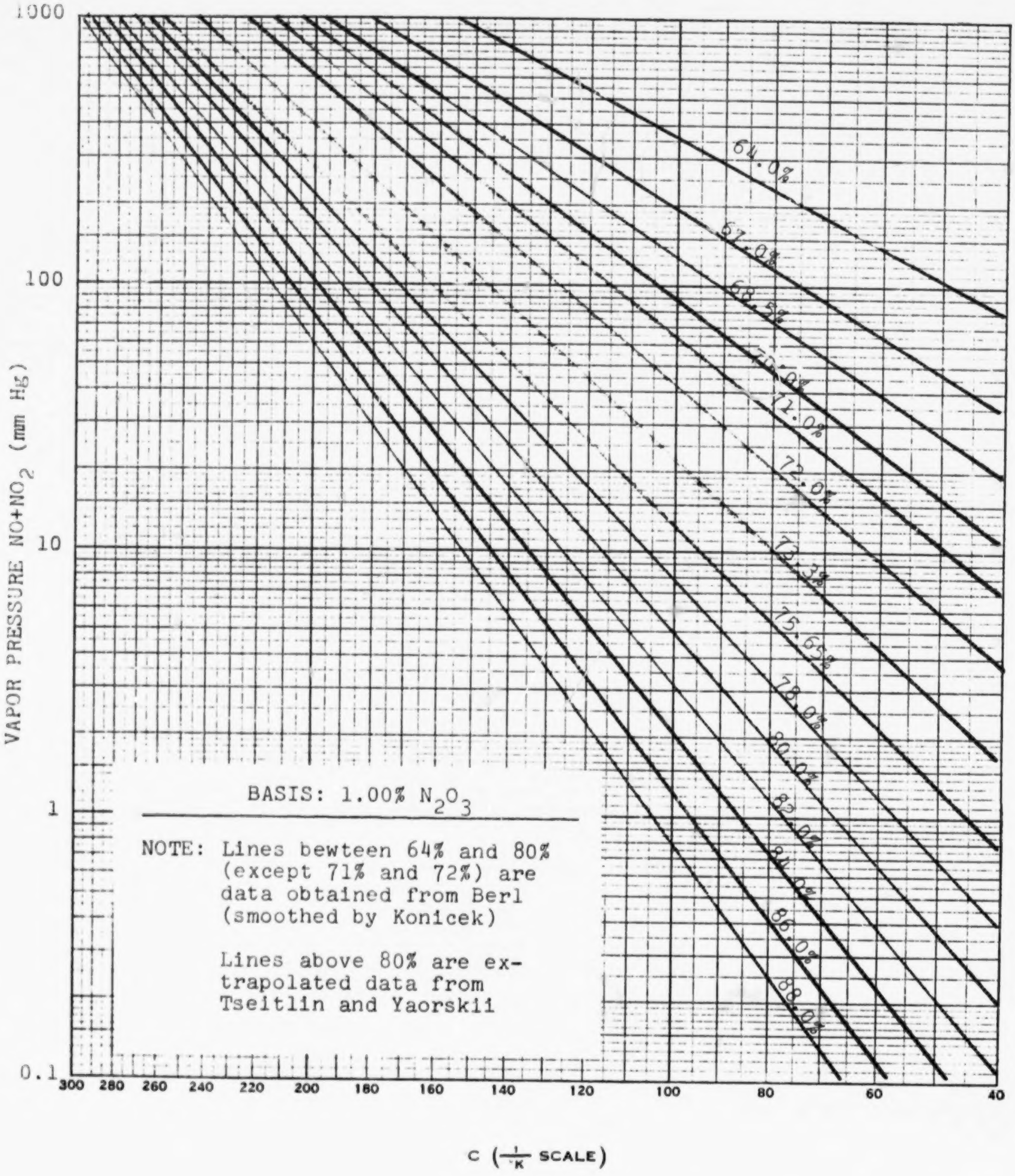
The design calculations given in this report were based on the vapor pressure data given in Figure 29.

C. Absorption Studies of NO and NO_2 into Sulfuric Acid

A laboratory absorption column was constructed to test the kinetics of absorption for NO and NO_2 into H_2SO_4 and to compare experimental absorption efficiencies with predicted efficiencies using vapor pressure data. Figure 30 is a schematic representation of the column. Two gas cylinders were used, one containing nitrogen and the other NO, NO_2 and N_2. The amount of gas fed from each cylinder was adjusted to provide NO and NO_2 vapor pressures of about 3 mm Hg each. These gases then passed into a mixing chamber to insure that the gas fed to the column would be homogeneous. The gas then passed through an electrically heated tube and into the bottom of the column. The column and acid reservoir were heated by exterior heating tapes, and insulated with 1/2 in. - 1 in. Pyrex wool. A description of the procedure used in this study is given in Appendix 9.

Table 5 is a summary of the data obtained from this study. Eight runs were made - the first three using a column packed with 1/2 in. Raschig rings, and the last five with a column packed with cut Pyrex tubing. This tubing consisted of about equal portions of 5 mm and 6 mm tubing cut to 5 mm and 6 mm lengths respectively.

Examination of the data revealed that the efficiency of the 1/2 in. Raschig rings to remove NO + NO_2 from the gas was about an order of magnitude less than the cut Pyrex tubing.



BASIS: 1.00% N_2O_3

NOTE: Lines bewteen 64% and 80% (except 71% and 72%) are data obtained from Berl (smoothed by Konicek)

Lines above 80% are extrapolated data from Tseitlin and Yaorskii

Figure 29. Adjusted Vapor Pressure of NO and NO_2 Over Nitrose

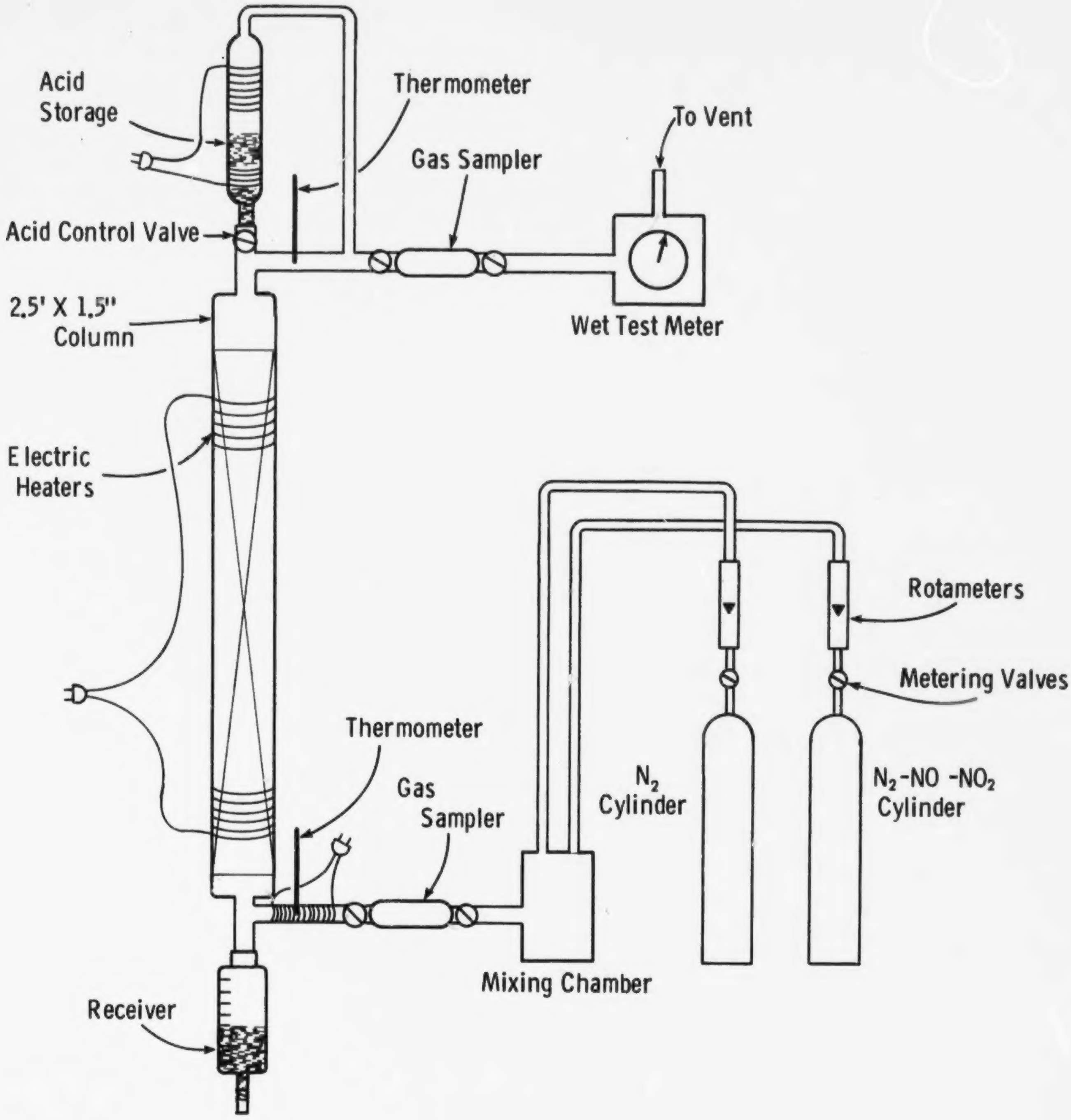

Acid Storage
Acid Control Valve
2.5' X 1.5" Column
Electric Heaters
Thermometer
Gas Sampler
To Vent
Wet Test Meter
Rotameters
Metering Valves
N_2 Cylinder
N_2-NO -NO_2 Cylinder
Thermometer
Gas Sampler
Mixing Chamber
Receiver

Figure 30. Absorption Studies Apparatus

Table 5

SUMMARY OF LABORATORY N_2O_3 ABSORPTION STUDIES

Estimated NO + NO_2 Press (mmHg)		NO + NO_2 Removal (%)	Approx. Flow Rate		Temperatures (°C)				Acid Conc. (% H_2SO_4)
Inlet	Outlet		Gas cc/Min	Acid cc/Min	Gas In	Gas Out	Acid In	Acid Out	
1.10	1.00	9.1	12000	15	119	117	129	75+	80
0.14	0.138	1.0	12000	80	120	126	110	-	80
3.8	3.4	10.5	12000	100	126	122	112	-	80
3.8	1.2	68.4	6000	80	26	26	26	~26	80
3.8	2.1	44.8	6000	33	26	26	26	~26	80
8.8	4.3	52.3	12000	35	82	75	79	-	85
3.78	1.41	62.7	12000	55	25	25	25	~25	85
4.82	0.74	85.0	12000	60	110	110	112	-	85

In an attempt to define the cause of the poor NO_x absorption, a gas sample of the N_2-NO-NO_2 mixture was taken and submitted to I.R. analysis. The analysis indicated that the sample had a respective gas ratio of 2:1:0.4 as NO_2/NO/N_2O. This unexpected appearance of N_2O in low concentration was found to be a result of using a very low grade NO supply. The NO cylinder used to blend the mixture contained about 25% N_2O and about 10% NO_2. Thus, of the total NO and NO_2 present, only 50% existed as a 1:1 ratio of NO to NO_2.

Since the removal of NO + NO_2 from flue gas is optimum with a 1:1 ratio of NO to NO_2, and falls off sharply as the ratio differs, it is not surprising that the average removal of NO + NO_2 was about 63% (avg. of last 5 runs).

Although the absorption studies did not show the desired 99.6% NO_x removal, they did point out the necessity of maintaining a 1:1 mole ratio of NO to NO_2. If this ratio is not maintained closely, the recovery of NO + NO_2 will be severely reduced.

D. Proposed SO_x-NO_x (SONOX) Removal Process Description

1. General Description

Utilizing the data gathered during our laboratory investigation of the dual purpose removal system, a process design was developed as shown in Figure 31. In this process, flue gas enters the bottom of a trifunctional absorption tower. In the bottom section flue gas is dewatered to ∿0.2% to 0.5% H_2O and cooled to 170°F by countercurrent contact with 160°F, 84% H_2SO_4. The acid is then diluted from 84% to about 81% and heated to about 290°F. The cooled flue gas then enters the middle section of the tower where recycle NO_2 is added. The NO_2 oxidizes SO_2 to SO_3 and the resulting NO reacts with residual NO_2 to form N_2O_3. The heat of reaction raises the gas temperature about 20°F while the SO_3 and N_2O_3 are absorbed in 80% H_2SO_4 at 190°F. The flue gas then enters the third section of the tower where it contacts the acid removed from the bottom section. The gas becomes humidified and heated while the acid is reconcentrated to 84% and cooled to about 160+°F. The acid may have to pass through a cooler to bring the temperature back to 160°F, unless there is evaporative cooling.

The acid removed from the middle section passes through a heat exchanger and into a stripping tower. Here the dissolved N_2O_3 is stripped from the acid at 338°F with hot gas. The denitrated acid leaves the stripper, passes through the heat exchanger, a cooler, and back to the middle section of the absorption tower. A small product stream is then removed beyond the heat exchanger. The stripper exit gas enters an oxidation chamber which provides sufficient time to effect 80+% conversion of NO to NO_2.

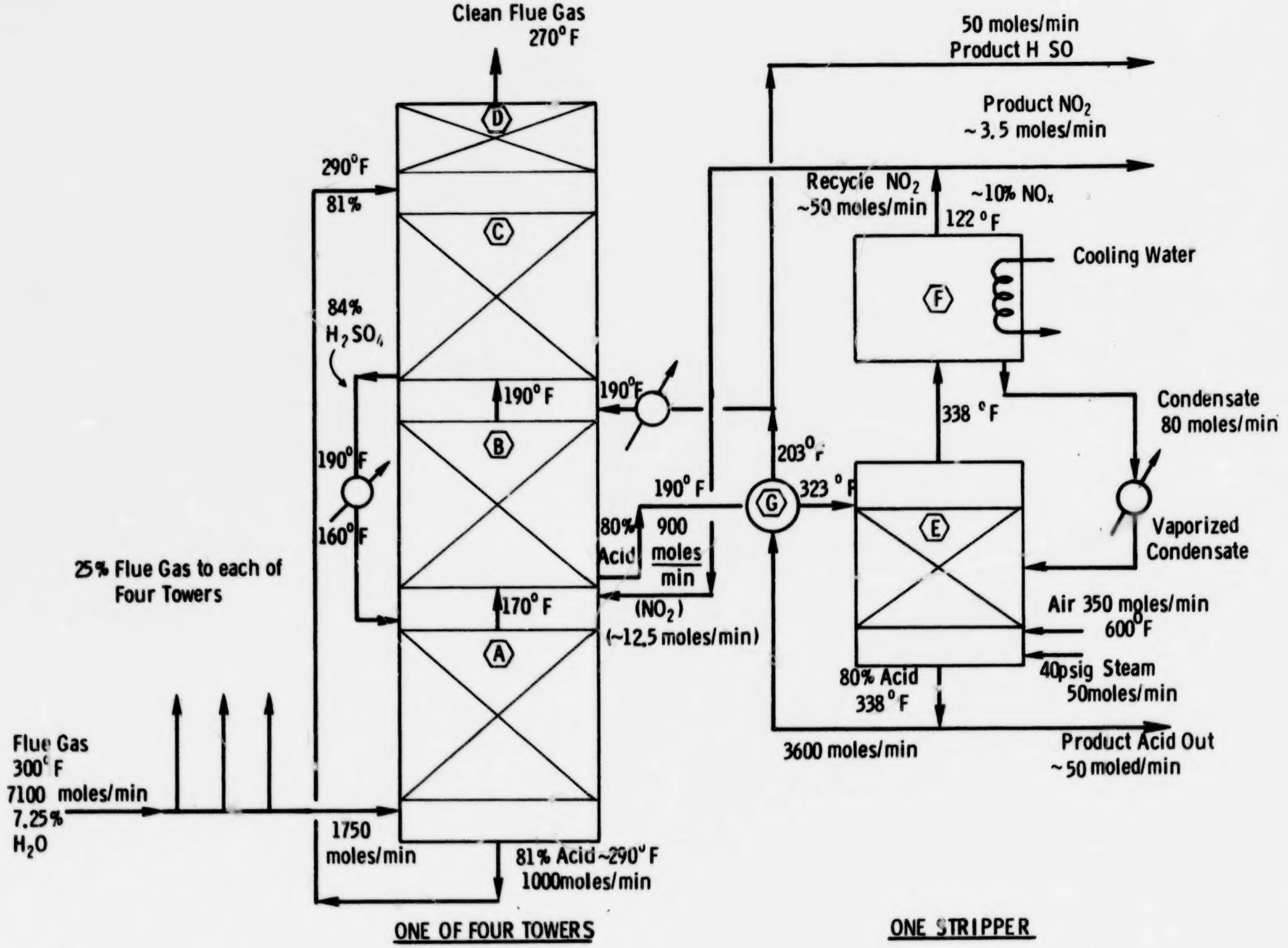

Clean Flue Gas
270°F
D
C
B
A
290°F
81%
84%
H2SO4
190°F
160°F
190° F
170° F
190°F
80%
Acid
900
moles
min
190° F
(NO2)
(~12.5 moles/min)
25% Flue Gas to each of
Four Towers
Flue Gas
300°F
7100 moles/min
7.25%
H2O
1750
moles/min
81% Acid ~290°F
1000moles/min
ONE OF FOUR TOWERS
50 moles/min
Product H SO
Product NO2
~3.5 moles/min
Recycle NO2
~50 moles/min
~10% NOx
122 °F
Cooling Water
F
338 °F
Condensate
80 moles/min
203°F
323 °F
G
E
Vaporized
Condensate
Air 350 moles/min
600°F
40psig Steam
50moles/min
80% Acid
338 °F
3600 moles/min
Product Acid Out
~50 moled/min
ONE STRIPPER

Figure 31. Process Design Schematic

Water vapor is condensed by cooling the gas to 122°F with water. The NO_2-rich gas stream, minus a small product stream, is then recycled to the middle section of the tower. The condensate from the oxidizer is revaporized and fed back to the stripper. In addition, make-up water is added to the stripper as steam.

2. Trifunctional Absorption Tower

a. Bottom Section of Absorption Tower

Vapor pressure studies on the system H_2SO_4-H_2O-N_2O_3 revealed the desirability of operating the absorption section of the tower at as low a temperature as possible and with an acid concentration of 80+%. In order to meet this requirement, the flue gas must be cooled to a suitable temperature (∿170°F) and must be dewatered to the equilibrium composition of H_2O vapor over 80% sulfuric acid at ∿190°F. The requirement that the gas must be dry arises from the fact that absorption of H_2O into the acid would be accompanied by a decrease in acid concentration and a rise in temperature from the heat of absorption - both detrimental to NO + NO_2 absorption.

The following assumptions were made in designing this section of the tower:

- 1.36 pounds of 84% H_2SO_4/pound of flue gas
- The temperature of the acid leaving the tower will be 10°F cooler than the entering flue gas temperature

b. Middle Section of Absorption Tower

In this section the SO_2 in the flue gas is oxidized to SO_3 by NO_2 (obtained from the recycle stream), thereby permitting removal of the sulfur as H_2SO_4. The amount of NO_2 recycled is controlled to affect a 1:1 ratio of NO to NO_2 after all the SO_2 is oxidized. The temperature of the recycle NO_2 stream is about 122°F and the heat of SO_2 reaction is sufficient to affect a 20°F rise in the flue gas temperature. Eighty (80) percent H_2SO_4 is used to scrub the NO + NO_2 gases from the flue gas. At these operating conditions, approximately 0.88 pounds of acid/pound of gas will remove 99.6% of the NO + NO_2 with 15 theoretical trays. The flue gas leaving this section contains about 0.25% H_2O, 0.003% SO_2, and about 0.005% NO_x, and the acid leaving this section contains about 1.08 wt% N_2O_3 (3.92% $HNSO_5$).

Here, the following assumptions were made:

- The oxidation of SO_2 to SO_3 is instantaneous
- Fifteen theoretical trays are desired
- No oxidation of NO takes place in the absorber.

c. Top Section of Absorption Tower

The function of this section is to utilize the dry clean flue gas to concentrate sulfuric acid from 81% to 84%. As the 81% acid enters the top of the section (from the bottom of the bottom section) at 690°F, the gas passes countercurrent to the acid and removes H_2O from the acid to an extent limited by the vapor pressure of H_2O over sulfuric acid. The gas leaving this section contains 6.9% H_2O and is at a temperature of 270°F. The 84% acid is cooled to 190°F. The acid then passes through a cooler where it is cooled to 160°F before it enters the bottom section.

Here, the following assumptions were made:

- The exit gas H_2O composition is within 80% of the H_2O composition in equilibrium with 81% acid at 290°F.
- The exit acid temperature will equal the inlet gas temperature.

3. Acid Demister

Function of the acid demister is obvious.

4. Stripper

The function of the stripper is to remove 99.7% of the N_2O_3 from the sulfuric acid by countercurrent scrubbing with air at an elevated temperature. Although four or more absorption towers (depending upon the diameter of each tower) are required, only one stripping tower is required. The combined acid streams from the absorbers enter the top of the stripper. Heat is added to the stripper in two ways. Air, at 565-600°F, is blown through the stripper adding 0.7×10^6 BTU/min to the acid. Steam (40 psig) adds heat to the acid by the heat of H_2O condensation and by the heat of H_2SO_4 dilution. The amount of steam added to the acid is equal to the amount of water present in the product acid plus the amount of water vapor present in the NO_2 product stream. This amounts to $\sim$50 moles of H_2O/minute. In addition, the condensate removed from the NO oxidizer is vaporized and fed back to the stripper. This amounts to $\sim$80 moles/min. By raising the acid temperature from 190°F to 338°F, and by lowering the acid concentration from 80.0% to 79.5%, the vapor pressure of $NO + NO_2$ is more than 30 times higher (over sulfuric acid) than it is in the absorber. Therefore, less than 5% of the flue gas flow rate is required to strip out the $NO + NO_2$. This amounts to about 350 moles of air per minute.

Assumptions made for stripping unit:

- The desired stripper temperature is 338°F
- The water vapor in the stripper exit gas is in equilibrium with 80% H_2SO_4 at 338°F.

5. NO Oxidizer

The function of the NO oxidizer is to provide sufficient residence time to allow the oxidation of NO to take place. Only one tower (about 35' x 30' diameter) is required. This provides 9 sec. contact time.

Assumptions made in this unit:

- 80+% conversion of NO is desired
- The gas is cooled to 122°F
- The reaction constant is 1.5×10^4 (l^2/mole^2·sec).

6. Acid-Acid Heat Exchanger

The function of the acid-acid heat exchanger is obvious. The size of the heat exchanger (surface area) depends upon the heat transfer coefficient and the ΔT. For an assumed heat transfer coefficient of 150 BTU/hr·ft^2·°F and a ΔT of 14°F, the required surface area is 345,000 ft^2.

Assumptions made for acid-acid heat exchanger:

- Temperature driving force is 14°F
- Heat transfer coefficient is 15 BTU/hr·ft^2·°F.

7. Heat and Material Balances

The material balance for this process is given in Table 6 . The flow rate of each compound in a given stream is shown in lb-moles/-min. The temperature and pressure of each stream is included if significant.

E. Comparison Between Tyco and Monsanto Modified Chamber Process

1. General Description of Process Flow Differences

The description of the Tyco modified chamber process was taken directly from a report issued by Tyco representatives at the Second Annual Control Process Contractors' Meeting (NAPCA) held on June 11-13, 1969, in Cincinnati, Ohio. A copy of that report is included in Appendix VIII.

The Tyco process basicly rests on two important design features: (1) the absorption of SO_3 and N_2O_3 ($NO + NO_2$) is accomplished in an absorption tower operating isothermally at 250°F using 80% H_2SO_4, (2) the absorbed N_2O_3 ($HNSO_5$) is oxidized in the liquid phase over a charcoal catalyst and the resulting NO_2 is removed by the gas sweeping through the column.

Table 6

HEAT AND MATERIAL BALANCE - HIGH TEMPERATURE STRIPPER

Stream	N_2	O_2	CO_2	H_2O	SO_2	NO_2	NO	H_2SO_4	N_2O_3	Temp. (°F)	Press. (mm Hg)	Comments
Flue Gas	5318	199	1044	515	21.3	0.35	3.20	--	--	300	785	
Gas Exit BTM	5318	199	1044	21	21.3	0.35	3.20	--	--	170	780	
Gas ABS Exit	5578	258	1044	21	0.3	0.17	0.17	--	--	190	775	
Clean Flue	5578	258	1044	515	0.3	0.17	0.17	--	--	270	770	
Recycle NO_2	260	59	--	28.9	--	45.45	5.05	--	--	122	790	
Prod. NO_2	16.5	3.7	--	1.8	--	2.88	0.32	--	--	122	790	
Oxidizer Eff.	276.5	62.8	--	30.7	--	48.33	5.37	--	--	122	790	Remove 2.86x10^6 Btu/min
Stripper Gas Out	276.5	73.5	--	112.3	--	26.85	26.85	--	--	338	800	
Strip Air	276.5	73.5	--	--	--	--	--	--	--	565	~900	
ABS BTM Acid Out	--	--	--	3106	--	--	--	2483	--	290	--	
ABS Top Acid Out	--	--	--	2612	--	--	--	2433	--	160$^+$/ 100	--	Cooler may be required
ABS Feed Acid	--	--	--	2066	--	--	--	1504	0.08	203/ 190	--	
ABS Acid Out	--	--	--	2075	--	--	--	1525	26.93	190/ 323	--	
Strip Acid Out	--	--	--	2094	--	--	--	1525	0.08	338/ 203	--	
Prod. Acid Cond.	--	--	--	28.8	--	--	--	21.0	--	203	--	
Oxidizer H_2O	--	--	--	81.6	--	--	--	--	--	122/ 380	40 psig	} ~$800,000/yr
Make-Up H_2O	--	--	--	51.6	--	--	--	--	--	380	40 psig	

Of the two features the second is more important. It makes it possible to operate the stripper at the same temperature as the absorber. Thus, there is no necessity to heat the acid in order to raise the N_2O_3 vapor pressure and permit desorption, and later cool it to the absorber temperature. The rest of the process consists of (1) recovering nitric and sulfuric acids, and (2) preparing the flue gas to enter the absorption tower by cooling to 250°F and reacting NO_2 with SO_2.

The Monsanto process differs from the Tyco process on both important design features. The absorption tower is trifunctional rather than monofunctional. In the first section of the tower the gas is cooled to about 170°F and dried to approximately 0.2-0.5% H_2O with 84% sulfuric acid. In the second section, NO_2 is added, oxidizing the SO_2 to SO_3 and the SO_3 plus NO and NO_2 are absorbed with 80% H_2SO_4 at 190°F. In the third section the flue gas is warmed and moistened by passing through the hot, humid acid removed from the bottom of the first section.

The stripper is also different. Assuming that neither charcoal or any other catalyst will effect the liquid phase oxidation of NO, the recovery of NO + NO_2 is accomplished by raising the acid temperature from 190°F to 338°F. At this temperature, the vapor pressure of NO + NO_2 is about 30 times higher than it was at 190°F, the absorbing temperature. Thus, the stripping of NO = NO_2 should be accomplished with less than 5% of the flue gas volume.

2. Detailed Process Comparison

Table 7 is a direct comparison between the Tyco and Monsanto processes. The comparison is made as the two processes were described. Tyco's stripper is catalytic and Monsanto's stripper is high temperature. The required absorption acid flow rates were calculated using the vapor pressure data shown in Figure 29 as a common basis. The major differences between the two processes are the following:

- Tyco process requires about twice the acid flow rate in the absorber as Monsanto's process
- Monsanto process is circulating 1.08 times as much acid as Tyco process
- Monsanto absorption towers will probably cost 2 to 2.5 times as much as Tyco towers
- Monsanto absorption tower is about 3 times higher than Tyco towers
- Monsanto process uses 24,000 GPM cooling water while Tyco uses 17,000 GPM.

Table 7

COMPARISON OF MONSANTO AND TYCO PROCESSES (AS DESIGNED)

	Subject	Monsanto	Tyco
1.	Gas Cooling	Uses a flue gas cooler to remove 1.3×10^6 Btu/min as low-grade steam Area of heat transfer = 90,000 ft^2 (cools gas to $\sim$278°F)	Cools all flue gas to 250°F; removes heat of SO_2 oxidation; removes heat of NO oxidation Heat removal = 2.9×10^6 Btu/min - cooling 0.8×10^6 Btu/min - SO_2 ox. 0.6×10^6 Btu/min - NO ox.
2.	Product Acid Concentration	80%	80% (limited to 92% maximum)
3.	Relative required acid flow rate for N_2O_3 absorption	1.0 ($\sim$184,000 lbs/min)	2.0 ($\sim$384,000 lbs/min)
4.	Stripper Operation	Uses temperature increases to strip $NO+NO_2$. Air is used as stripping gas (possibly with some flue gas). No catalyst is assumed. Required gas rate is 350 moles (at least 120 must be air)	Uses charcoal as a catalyst to oxidize N_2O_3 to 2 NO_2. Flue gas is used to oxidize NO and strip NO_2 from acid. Requires minimum of 850 moles/min of flue gas to provide sufficient O_2 for oxidation (if no air is used)
5.	Stack Gas Exit Temperature	270+°F	250+°F
6.	NO Oxidation Chamber	A tower 30' Ø by 36' (provides $\sim$9 sec contact time)	None required if charcoal catalyzes NO oxidation in stripper.
7.	Total Relative Acid Circulation Rate (Absorber Stripper)	1.08 (have three separate absorption sections)	1.0 (one absorption section)
8.	SO_2 Reactor	Done in absorber	Done prior to entrance to absorber in a tower (unknown dimensions)
9.	Acid Heat Exchangers Required	One acid-to-acid exchanger with 327,000 ft^2	None
10.	Acid Coolers	8 (total 45,000 ft^2)	None
11.	Maximum $HNSO_5$ conc. in absorber (at minimum L/G)	6.08	1.34
12.	Relative Absorber Tower Construction Difficulty	2-2.5	1.0
13.	Stripping Tower Construction Difficulty	1.0	>1.0
14.	Catalyst Losses	None	There appears to be some indication that NO_2 oxidizes carbon to CO or CO_2. Since this would be accompanied by NO_2 reduction, additional oxygen is required.
15.	Pressure Drop by Flue Gas	$\sim$26" H_2O	$\sim$20" H_2O
16.	Cooling Water Requirements	24,000 GPM	17,000

- Monsanto process requires an acid-acid heat exchanger (345,000 ft^2) and 8 acid-water heat exchangers (total of 45,000 ft^2). Tyco process requires no acid heat exchangers.

3. Detailed Comparison Using Identical Strippers

If a catalyst does exist which will effect the oxidation of N_2O_3 to NO_2 in the stripper, then the absorber is no longer required. The process flow becomes much simpler. There is no need to have acid-acid heat exchange or acid coolers, and the absorption tower can be operated as a monofunctional tower. The dewatering and humidifying sections can also be eliminated.

The Monsanto process and the Tyco process thus become very similar. The major differences are the following:

- Monsanto oxidizes SO_2 in the absorber
  Tyco oxidizes SO_2 in a separate chamber
- Tyco process operates at 250°F requiring flue gas cooling
  Monsanto process operates at 300°F requiring flue gas cooling
- Tyco product acid concentration will be 80%
  Monsanto's will be 87%.

F. Remaining Questions to be Answered

- Will evaporative cooling eliminate the need to cool the acid leaving the third section of the absorption tower?
- What is the maximum gas flow rate that can be tolerated in the absorption tower?
- Will NO oxidation take place in the stripper and/or absorber and eliminate the need for an oxidizing chamber?
- What is the minimum acid rate required to cool and dewater the flue gas?
- Is it more economical to increase the size of the acid-acid heat exchanger or to increase the temperature of the stripping air?
- Can flue gas be used as part of the stripping air (and H_2O requirement)?
- Is it more economical to operate the stripper at high temperature and low air rate or low temperature and high air rate?

- What is the height of packing required in each of the three sections of the absorption tower and stripping tower?
- What will the pressure drop be through the absorption tower?
- Is it necessary to monitor the NO/NO_2 ratio in the absorption tower? If so, how?
- What materials of construction are required?
- Is there a catalyst that can be used in the stripper that will permit oxidation of N_2O_3 to NO_2 and thereby facilitate stripping of NO_x at lower stripping temperatures?

REFERENCES

1. Berl, Z. Anorg. Allgem. Chem. 202, 113-34 (1931).

2. Tseitlin and Yavorskii, Journal of Applied Chemistry/U.S.S.R. 39 (5) (1966).

VI. PROCESS DESIGN

A. General

As a result of laboratory testing of catalysts of various types, a process design evolved based upon commercial vanadia catalysts. It is necessary to note that the designs presented below were developed solely from laboratory data supplemented with pertinent information from the literature and various equipment vendors. There was no piloting of the processes under the contract. It is also necessary to note that the basic process proposed here and labeled MRC/NAPCA is superficially quite similar to published descriptions of Monsanto Company's Cat-Ox® process. The two were developed completely independently of each other. Published details of the Cat-Ox® process only appeared toward the end of the present design effort. Although such information was too late to be influential in the designs shown below, it did serve very conveniently as a means of checking the reasonableness of these designs at a number of points.

Four process designs are presented. The key step in each is conversion of SO_2 to SO_3 over a supported vanadia catalyst at 850°F. The basic process consists of such conversion followed by heat recovery steps and then condensation of the sulfuric acid produced for recovery. A minor departure from the basic derives from the available temperature of flue gas. This normally is about 300°F. for existing power boilers. The catalytic converter, however, requires feed gas at 850°F. Consequently, the basic process applied to an existing power plant requires adding provision for preheating the gas fed to the converter.

In applying the process to a proposed power plant, provision can be made in the power plant design to provide gas to the converter at 850° - 900°F. without the additional heating step.

A major departure in design, shown below, from the basic process consists in the mode of SO_3 recovery proposed by the Callery Chemical Company.

The four cases of process designs presented, then, are intended to provide a view of the basic process, with various modifications, under most probable applications.

Case I.	MRC/NAPCA process applied to a large new (1400 Mw) power plant (no separate preheat)
Case I-A.	High temperature oxidation by solid catalysis followed by reversible dry absorption of SO_3 (Callery Chemical Company modification)

Case II.	MRC/NAPCA process applied to a small (220 Mw) existing power plant (separate preheat)
Case III.	MRC/NAPCA process applied to the off-gas from a reverberatory furnace of a small copper smelter

Case I is illustrated in greater detail than the other three cases. Capital and operating cost estimates are presented for all four cases.

Cost estimates are based upon the following general assumptions for all four cases. Special assumptions pertinent to a particular process are presented along with the process descriptions below.

- Flue gas and off-gas analysis:

Component	Power Plant Flue-Gas (% by Volume)	Smelter Off-Gas (% by Volume)
N_2	74.9	76.75
CO_2	14.7	3.48
H_2O	7.25	8.94
O_2	2.8	9.38
SO_2	0.3	1.45
NO_x	0.05	--
Fly Ash	0.2 (by weight)	--

- Following ratio factors were used for estimating the fixed capital cost:

Piping	50% of purchased equipment cost (except for large new power plant facility)
Instruments	15% of purchased equipment cost
Insulation	12% of purchased equipment cost
Electrical	10% of purchased equipment cost
Building	10% of purchased equipment cost

Land and yard improvements	15% of purchased equipment cost
Utilities	15% of purchased equipment cost
Engineering & Construction	20% of physical plant cost
Contingency & Contractor's Fee	20% of direct plant cost

• Catalyst Life	5 years
• Catalyst Cost	$1.45/liter ($41/cu.ft.)

- Amount of vanadia catalyst is based on W/F - conversion profile for catalyst "A" at 850°F (Figure 32) plus 10% excess catalyst

• Size and shape of catalyst	3/8 in, cylinders
• Rate of Return	8% per year
• Direct Labor	$3.00/hr.
• Supervision	$7800 and $12,000 annually for first-line supervisors and area superintendents, respectively
• Maintenance	5% of the fixed capital investment
• Plant Supplies	15% of the maintenance cost
• Utilities	a) steam -- 50¢/1000 lb b) electricity -- $0.006/Kw-hr c) water -- raw (untreated) - 10¢/1000 gal process (treated) - 25¢/1000 gal recirculated cooling tower - 5¢/1000 gal d) compressed air -- 5¢/1000 CF
• Payroll Burden	20% of direct labor and supervision
• Plant Overhead	50% of labor, maintenance and supplies

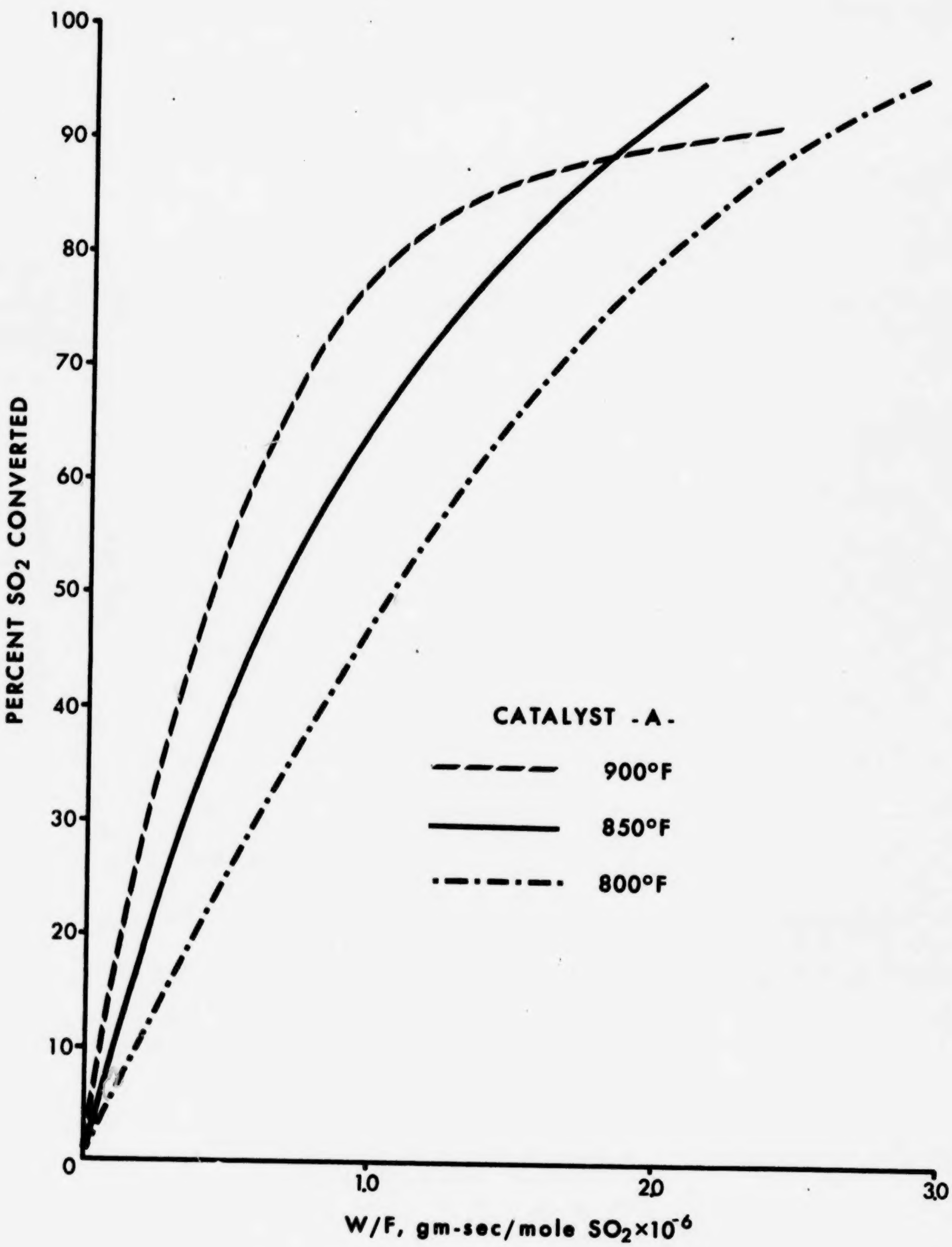


Figure 32. W/F-Conversion Profiles for Catalyst 'A'

• Depreciation	10% of the fixed capital investment
• Taxes	2% of the fixed capital investment
• Insurance	1% of the fixed capital investment

Major equipment costs for a large new power plant facility (MRC/NAPCA process) were substantiated by quotations from equipment vendors. For other cases, equipment costs were estimated by using cost data gathered by Monsanto's Central Engineering Department and cost data from authoritative publications. Piping cost for the large new power plant facility was estimated from labor and material take-off. For this type of estimation, process flow sheet (Figure 33) and plan and elevation drawings (Figures 34, 35) were used.

Cost of equipment or other facilities normally required for usual power plant operation is not incorporated in the capital investment or operating cost estimates. Only the additional and/or incremental costs for air pollution control are estimated.

B. Case I. MRC/NAPCA Process - New 1400 Mw Plant

For a new power plant, the design assumes the availability of flue gas at a temperature of 850° - 900°F. A flow diagram for one train of this process is shown in Figure 33. There are four trains for the 1400 Mw station. Table 8 presents an overall material balance and Table 9 shows the balance for a single train.

Hot gas from the boiler is relieved of 99+% of its dust burden in a high temperature, electrostatic precipitator. The near perfect efficiency of fly ash removal is necessary to minimize clogging, or blinding, of the catalyst bed in the next step. The gas then flows through fixed beds of vanadia catalyst where 90% of the sulfur dioxide is oxidized to sulfur trioxide. The design of the catalytic converter required optimizing pressure drop, through the catalyst bed, with tower diameter. Tower diameter establishes gas velocity which affects pressure drop. The latter relates directly to operating cost. The converter design evolved consists of a set of shallow catalyst beds in parallel. Gas flows up through the beds, as indicated in Figure 35, to facilitate periodic cleaning beds to remove fly ash. There are four such converters, each with 13 beds for the gas handling capacity at this station size. The program employed for converter optimization is given in Appendix IV to this volume. Further, in Appendix III are the program and results establishing the relationship between catalyst particle geometry and pressure drop through the catalyst bed.

Gas leaving the converter is then cooled to about 500°F. In a new power plant cooling is accomplished by stepwise passage through an

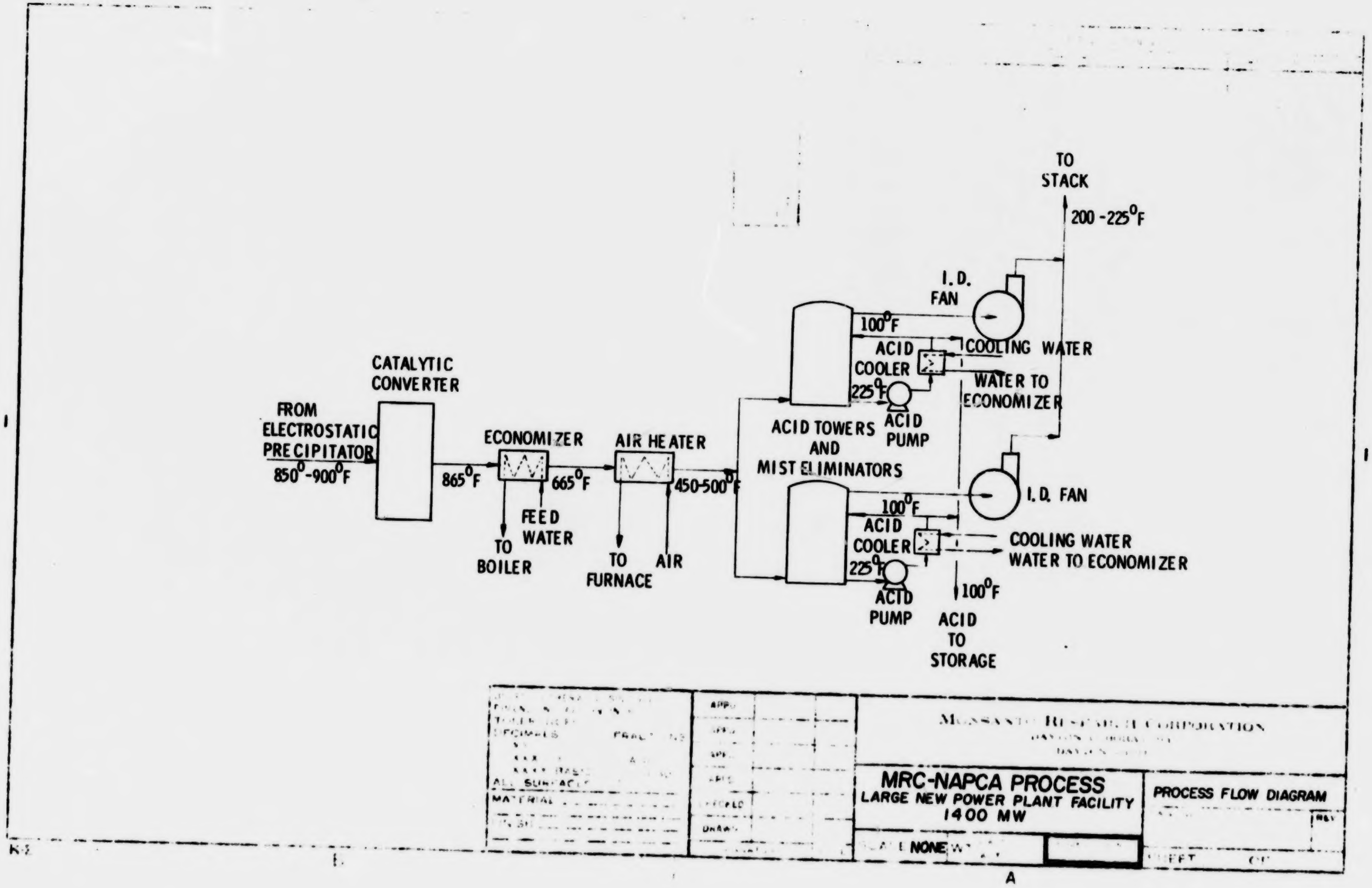

FROM ELECTROSTATIC PRECIPITATOR
850°-900°F
CATALYTIC CONVERTER
865°F
ECONOMIZER
665°F
TO BOILER
FEED WATER
AIR HEATER
450-500°F
TO FURNACE
AIR
ACID TOWERS AND MIST ELIMINATORS
100°F
ACID COOLER
225°F
ACID PUMP
I. D. FAN
COOLING WATER
WATER TO ECONOMIZER
I. D. FAN
COOLING WATER
WATER TO ECONOMIZER
100°F
ACID TO STORAGE
TO STACK
200-225°F
MONSANTO RESEARCH CORPORATION
MRC-NAPCA PROCESS
LARGE NEW POWER PLANT FACILITY
1400 MW
PROCESS FLOW DIAGRAM
SCALE NONE
A

Figure 33. MRC-NAPCA Proces[illegible] Large New Power Plant Facility, 1400 MW Process Flow Di[illegible]am

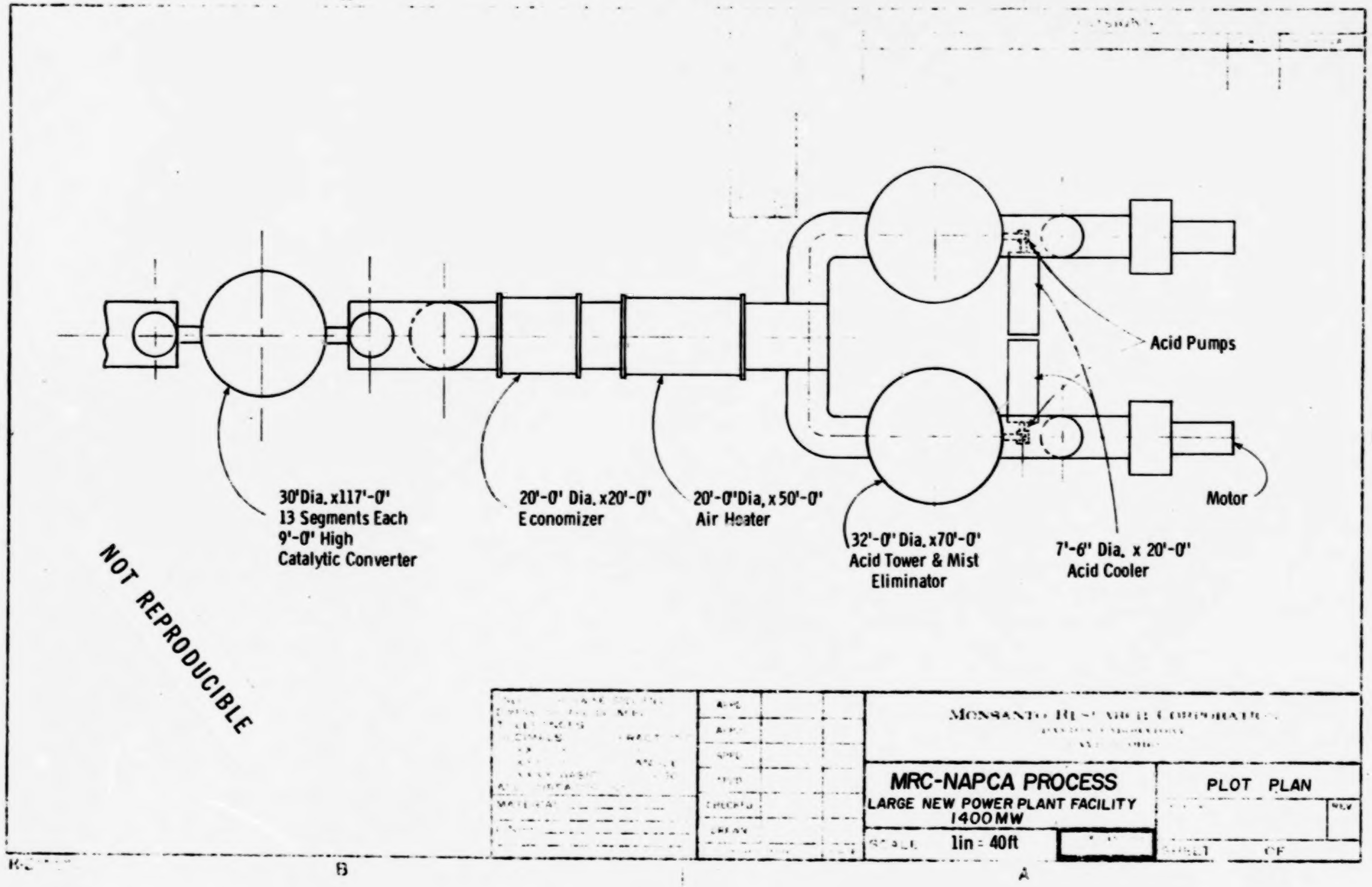

30'Dia. x117'-0" 13 Segments Each 9'-0" High Catalytic Converter
20'-0" Dia. x20'-0" Economizer
20'-0"Dia. x 50'-0" Air Heater
32'-0" Dia. x70'-0" Acid Tower & Mist Eliminator
7'-6" Dia. x 20'-0" Acid Cooler
Acid Pumps
Motor
NOT REPRODUCIBLE
MONSANTO RESEARCH CORPORATION
MRC-NAPCA PROCESS
LARGE NEW POWER PLANT FACILITY 1400MW
PLOT PLAN
1in = 40ft
B
A

Figure 34. MRC-NAPCA Process, Large New Power Plant Facility, 1400 MW Plot Plan

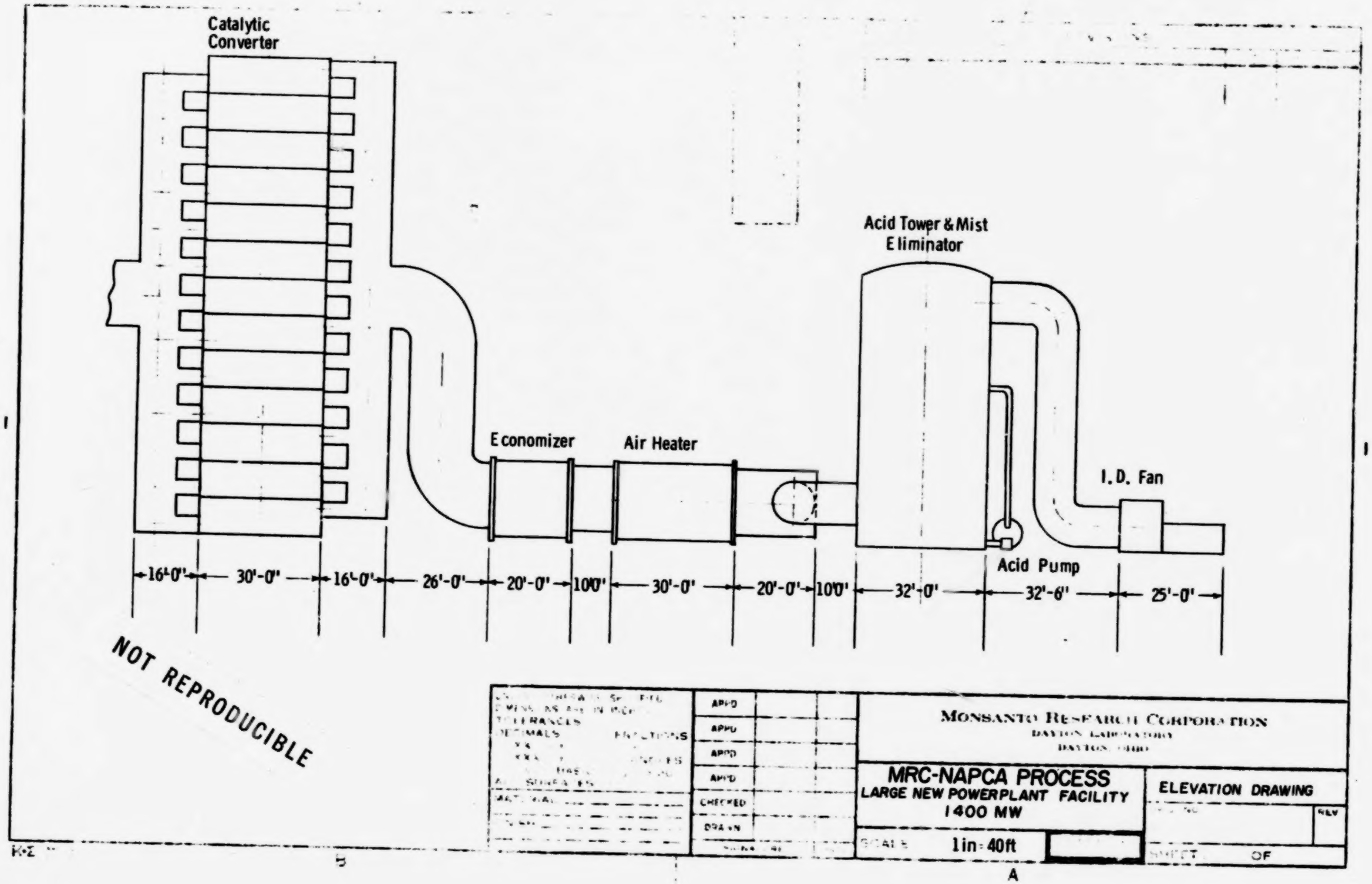

Catalytic Converter
Economizer
Air Heater
Acid Tower & Mist Eliminator
Acid Pump
I.D. Fan
16'-0"
30'-0"
16'-0"
26'-0"
20'-0"
10'0"
30'-0"
20'-0"
10'0"
32'-0"
32'-6"
25'-0"
NOT REPRODUCIBLE
APPD
APPD
APPD
APPD
CHECKED
DRAWN
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
MRC-NAPCA PROCESS
LARGE NEW POWERPLANT FACILITY
1400 MW
ELEVATION DRAWING
SCALE
1in=40ft
REV
SHEET
OF
A

Figure 35. MRC-NAPCA Process, Large New Power Plant Facility, 1400 MW Elevation Drawing

Table 8

SO_2 REMOVAL FROM FLUE GAS

CATEGORY: Large New Power Plant Facility

PROCESS FLOW SHEET

NAME OF PROCESS: MRC-NAPCA Process   MW: 1400   FLUE GAS RATE: 2.5 x 10^6 SCFM

Process Stream	Flow			Temp.	Composition in Weight Percent								
	lb/hr	GPM	SCFM	°F	N_2	CO_2	H_2O	O_2	SO_2	NO_x	SO_3	H_2SO_4	CH_4
from boiler to converter	11.81x10^6	---	2.50x10^6	850-900	70.27	21.66	4.37	3.00	0.64	0.05	---	---	---
from converter to economizer	11.81x10^6	---	2.49x10^6	865	70.27	21.66	4.22	2.86	Trace	0.05	Trace	0.84	---
from economizer to air heater	11.81x10^6	---	2.49x10^6	665	70.27	21.66	4.22	2.86	Trace	0.05	Trace	0.84	---
from air heater to acid tower	11.81x10^6	---	2.49x10^6	450-500	70.27	21.66	4.22	2.86	Trace	0.05	Trace	0.84	---
from acid tower to stack	11.67x10^6	---	2.47x10^6	200-225	71.07	21.91	3.98	2.89	Trace	0.05	Trace	Trace	---
from acid tower to storage	13.26x10^4	195.67	---	100	---	---	25.00	--	---	--	---	75.00	---

Table 9

SO_2 REMOVAL FROM FLUE GAS

CATEGORY: Large New Power Plant Facility

PROCESS FLOW SHEET

NAME OF PROCESS: MRC-NAPCA Process

FLUE GAS RATE: 62.5×10^4 SCFM

Process Stream	Flow			Temp.	Composition in Weight Percent								
	lb/hr	GPM	SCFM	°F	N_2	CO_2	H_2O	O_2	SO_2	NO_x	SO_3	H_2SO_4	CH_4
from boiler to converter	2.95×10^6	---	62.5×10^4	850-900	70.27	21.66	4.37	3.00	0.64	0.05	---	---	---
from converter to economizer	2.95×10^6	---	62.3×10^4	865	70.27	21.66	4.22	2.86	Trace	0.05	Trace	0.84	---
from economizer to air heater	2.95×10^6	---	62.3×10^4	665	70.27	21.66	4.22	2.86	Trace	0.05	Trace	0.84	---
from air heater to "tee"	2.95×10^6	---	62.3×10^4	450-500	70.27	21.66	4.22	2.86	Trace	0.05	Trace	0.84	---
from "tee" to acid tower	1.48×10^6	---	31.2×10^4	450-500	70.27	21.66	4.22	2.86	Trace	0.05	Trace	0.84	---
from acid tower to stack	1.46×10^6	---	30.9×10^4	200-225	71.07	21.91	3.98	2.89	Trace	0.05	Trace	Trace	---
from acid tower to storage	1.66×10^4	24.46	---	100	---	---	25.00	--	---	--	---	75.00	---

NOTE: Large stream of 2.5×10^6 SCFM is divided into four parallel streams economizer and air heater. The economizer takes heat from the flue gas to heat boiler feed water while an air preheater is used to recover more heat from the flue gas by heating the air prior to its entry into the boiler firebox. Further cooling and condensation of sulfuric acid mist is accomplished in packed acid towers which operate in conjunction with acid coolers. Heat recovered in the acid coolers is used to preheat boiler feed water. The acid towers in this process, Figure 33, are reminiscent of the absorbers in a contact sulfuric acid plant. In the latter, however, the primary function is truly absorption, i.e., of SO_3 into slightly diluted sulfuric acid where more sulfuric acid is formed. In the case of the flue gas process, sulfuric acid exists as such in the gas and will condense as a mist if the gas is cooled. Consequently, the main function of the acid towers here is to cool the flue gas to the dew point of the acid which then condenses into the liquid in the tower. The relationship of SO_3 in the flue gas to strength of the acid condensing is shown in Appendix 10 to this volume.

The fine sulfuric acid mist not retained in the acid tower is removed by high efficiency (about 95%) mist eliminators prior to discharge of the flue gas to the stack. Acid produced by this process is stored for shipment as a 75 - 80%, or fertilizer grade, sulfuric acid.

One of the major decisions in designing a process for hanging onto the end of a power plant is the capacity for which to design. In this case, we have designed for 100% capacity all of the time, knowing, however, that this may not be realistic. On the other hand, designing for a lesser capacity would mean sacrificing emission control during periods of peak capacity. In Figure 36 a scheme is presented which permits the process to be run at incremental capacities or at full capacity with only three of the four converters on line. Each converter has a 10% overdesign. All four heat-recovery trains are available at all times to minimize loss of thermal efficiency.

Figure 35 is an elevation view of one conversion train while Figure 34 is a plan view. Both figures give some idea of the size of the treatment plant.

Instrumentation for the MRC/NAPCA process is comparatively simple (Figure 37). Pressure drop through the catalytic converter indicates fly ash accumulation in the catalyst beds. Instruments and control equipment maintain proper temperature, pressure, draft and liquid flow rates to maximize treatment and power plant efficiency and minimize interference with the power plant operation.

Tables 10 through 14 present specifications for basic equipment employed in this Case I process design.

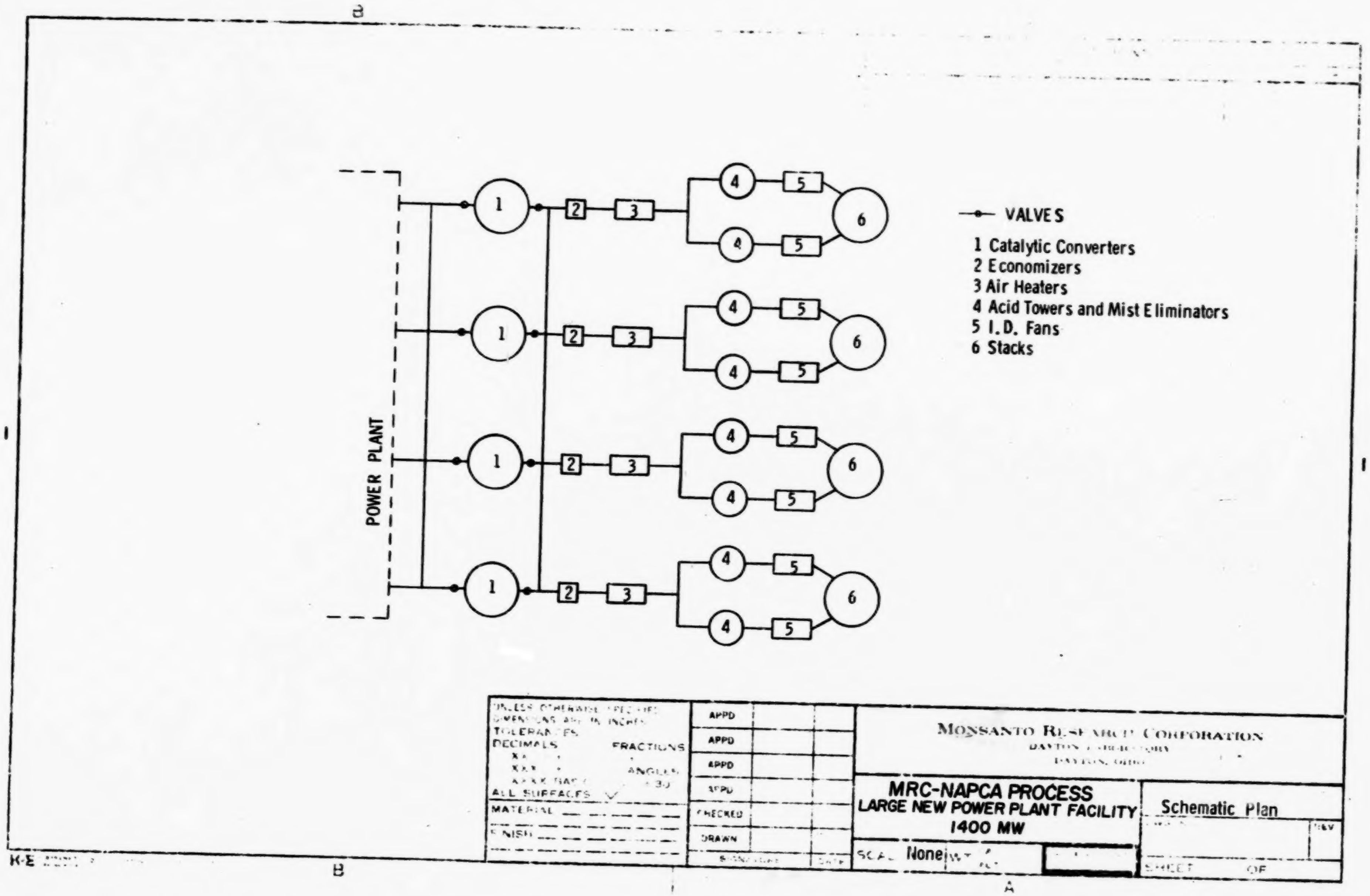

POWER PLANT
1
2
3
4
5
6
VALVES
1 Catalytic Converters
2 Economizers
3 Air Heaters
4 Acid Towers and Mist Eliminators
5 I.D. Fans
6 Stacks
MONSANTO RESEARCH CORPORATION
DAYTON, OHIO
MRC-NAPCA PROCESS
LARGE NEW POWER PLANT FACILITY
1400 MW
Schematic Plan
SCALE None
SHEET OF
APPD
CHECKED
DRAWN
MATERIAL
FINISH
ALL SURFACES
DECIMALS
FRACTIONS
ANGLES
TOLERANCES
B
A

Figure 36. MRC-NAPCA Process, Large New Power Plant Facility, 1400 MW Schematic Plan

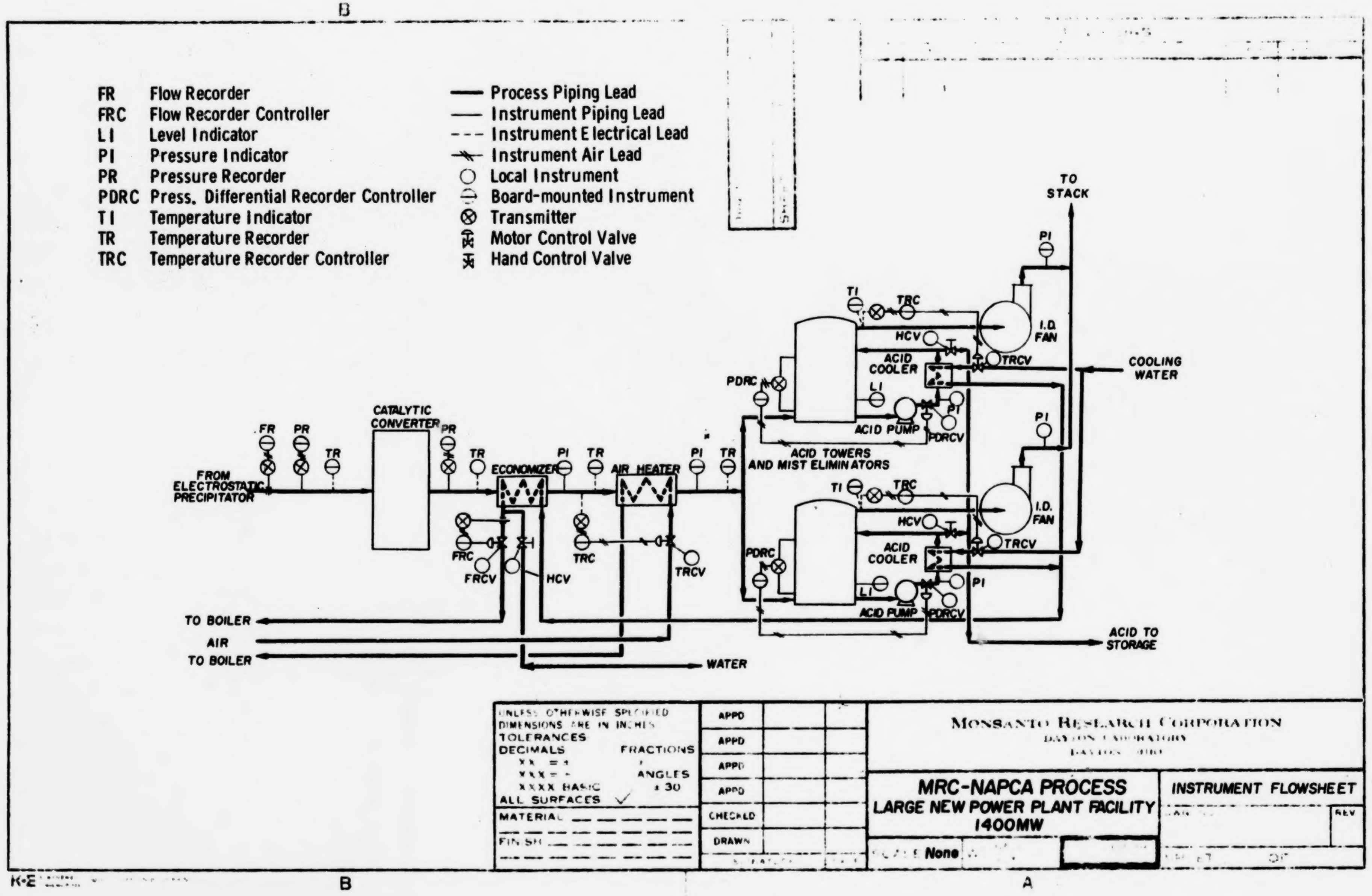

FR Flow Recorder
FRC Flow Recorder Controller
LI Level Indicator
PI Pressure Indicator
PR Pressure Recorder
PDRC Press. Differential Recorder Controller
TI Temperature Indicator
TR Temperature Recorder
TRC Temperature Recorder Controller
Process Piping Lead
Instrument Piping Lead
Instrument Electrical Lead
Instrument Air Lead
Local Instrument
Board-mounted Instrument
Transmitter
Motor Control Valve
Hand Control Valve
FROM ELECTROSTATIC PRECIPITATOR
CATALYTIC CONVERTER
ECONOMIZER
AIR HEATER
FRC
FRCV
HCV
TRC
TRCV
TO BOILER
AIR
TO BOILER
WATER
PDRC
ACID TOWERS AND MIST ELIMINATORS
TI
HCV
ACID COOLER
LI
ACID PUMP
PDRCV
I.D. FAN
TO STACK
COOLING WATER
ACID TO STORAGE
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES
TOLERANCES
DECIMALS
FRACTIONS
ANGLES
ALL SURFACES
MATERIAL
FINISH
APPD
CHECKED
DRAWN
MONSANTO RESEARCH CORPORATION
MRC-NAPCA PROCESS
LARGE NEW POWER PLANT FACILITY
1400MW
INSTRUMENT FLOWSHEET
SCALE None
REV
A
B

Figure 37. MRC-NAPCA Process, Large New Power Plant Facility, 1400 MW Instrument Flowsheet

Table 10

CATALYTIC CONVERTER

1. GENERAL

Number of reactors in parallel - 4
Number of catalyst beds in parallel in each reactor - 13
Overall height of each reactor - 117 ft.
Diameter of each reactor - 30 ft.
Height of each segment - 9 ft.
Height of each bed - 6-1/4 in.
Size and shape of catalyst - 3/8 in., cylinders
Total volume of catalyst - 20,000 cubic feet

2. OPERATING CONDITIONS OF EACH REACTOR

Total gas entering - 2.95 x 10^6 lb/hr
Inlet temperature - 850°F
Outlet temperature - 865°F
Operating pressure - Slightly below atmospheric
Superficial gas velocity through each bed - 3.22 ft/sec.
Pressure drop - 0.96 in. H_2O

3. MATERIALS OF CONSTRUCTION

Converter shell - Carbon steel
Supports, beams, grates - Carbon steel (SA-285 Grade C)
Blank plates between each segment - Cast iron

Table 11

ACID RECOVERY AND MIST COLLECTION TOWER

1. GENERAL

Number of towers in parallel - 8
Overall height of each tower - 70 ft.
Diameter of each tower - 32 ft.
Packed height in each tower - 16 ft.
Size and type of packing - 3" Intalox Saddles

2. OPERATING CONDITIONS OF EACH TOWER

Total gas entering - 1.48×10^6 lb/hr (31.2×10^4 SCFM)
Total liquid entering - 1.94×10^6 lb/hr (2,320 GPM)
Gas inlet and outlet temperatures - 500°F and 225°F
Liquid inlet and outlet temperatures - 100°F and 225°F
Operating pressure - Slightly below atmospheric
Pressure drop through the acid recovery tower - 8 in. H_2O
Pressure drop through the mist eliminator - 10 in. H_2O

3. MATERIALS OF CONSTRUCTION

Tower - Carbon-steel vessel with minimum of 4" of acid-proof brick lining.
Packing - Chemical stoneware
Mist element - Chemically resistant glass fibers

Table 12

ACID COOLER

1. GENERAL

Size - 7' - 6" Ø x 20'
Type - Shell and Tube
Sq. Ft. Surface/Shell - 27,750
Number of Units - 8

2. PERFORMANCE OF ONE UNIT

	Shell Side	Tube Side
Fluid Circulated	Water	75% Sulfuric Acid
Total Fluid Entering	1.125×10^6 lb/hr (2,250 GPM)	1.94×10^6 lb/hr (2,320 GPM)
Temperature In	80°F	100°F
Temperature Out	181°F	225°F
Pressure Drop	20 PSI	10 PSI

Heat Exchanged - 114×10^6 Btu/Hr
MTD (Corrected) - 25.2°F
Transfer Rate Service - 163 Btu/(Hr) (ft^2)(°F)

3. MATERIALS OF CONSTRUCTION

Tubes: Welded Carpenter 20
Shell: Carbon Steel

Table 13

ACID PUMP

1. GENERAL

Pump Type - Centrifugal
Number of Units - 8

2. OPERATING CONDITIONS OF EACH UNIT

Liquid Pumped: 75% Sulfuric Acid
Capacity, @ 225°F, Normal 2,300 GPM, Design 2,540 GPM
Specific Gravity @ 225°F - 1.67
Viscosity @ 225°F - 6 cps
Diff. Head - 65 ft.

3. MATERIALS OF CONSTRUCTION

Casing - Stainless Steel, Alloy 20
Impeller - Stainless Steel, Alloy 20
Shaft - Stainless Steel, Alloy 20
Packing - None

4. DRIVER DATA

Motor HP - 100, RPM - 1160
Phase - 3, Cycle - 60, Volts - 440

Table 14

INDUCED DRAFT FAN

1. GENERAL

Type of Fan - Double Inlet Centrifugal Fan
Number of Units - 8
Size: Height - 13 ft, Width - 18 ft, Length - 10 ft

2. OPERATING CONDITIONS OF EACH UNIT

Inlet Temperature - 225°F
Suction Pressure - 30 In. Water
Gas Density - 0.06 lb/ft^3
Capacity - 400,000 CFM @ 225°F and 14.7 psia

3. TYPE OF FLOW CONTROL

Discharge Damper

4. MATERIAL OF CONSTRUCTION

Carbon Steel

5. DRIVER DATA

Motor HP - 3,000, RPM - 1,200
Phase - 3, Cycle - 60, Volts - 2,300
Accessory - Brushless type exciter

In addition to the general assumptions previously cited, the following assumptions were also employed in the Case I capital and operating cost estimates:

• Flue Gas Rate	2.5 MM SCFM
• Size of Power Plant	1400 Mw
• Coal Required for Power Plant	580 tons/hr
• Operating Factor	330 days/year @ 100% capacity
• SO_2 Conversion	90%
• SO_3 Recovered as H_2SO_4	95%
• Flue Gas Temperature	850 to 900°F
• Cost of 3" Intalox Saddles	$\$4.55/ft^3$

Tables 15 through 18 show capital and operating cost estimates for Case I. Figure 38 shows the effect of product sale price on net operating cost.

C. Case I-A. Reversible Dry Absorption of SO_3

This case differs from Case I primarily in the mode of product recovery. In this process, sulfur dioxide in flue gas is first oxidized to sulfur trioxide over vanadia catalyst, as in Case I. However, the product sulfur trioxide is removed from the main gas stream by sorption on a dry medium, Na_2SO_4, at relatively high temperature. Desorption is effected at still higher temperature by decomposition of the sorption product. The reactions involved are:

$$SO_3 + Na_2SO_4 \overset{850°F}{=} Na_2S_2O_7$$

$$Na_2S_2O_7 \overset{1000°F}{=} Na_2SO_4 + SO_3$$

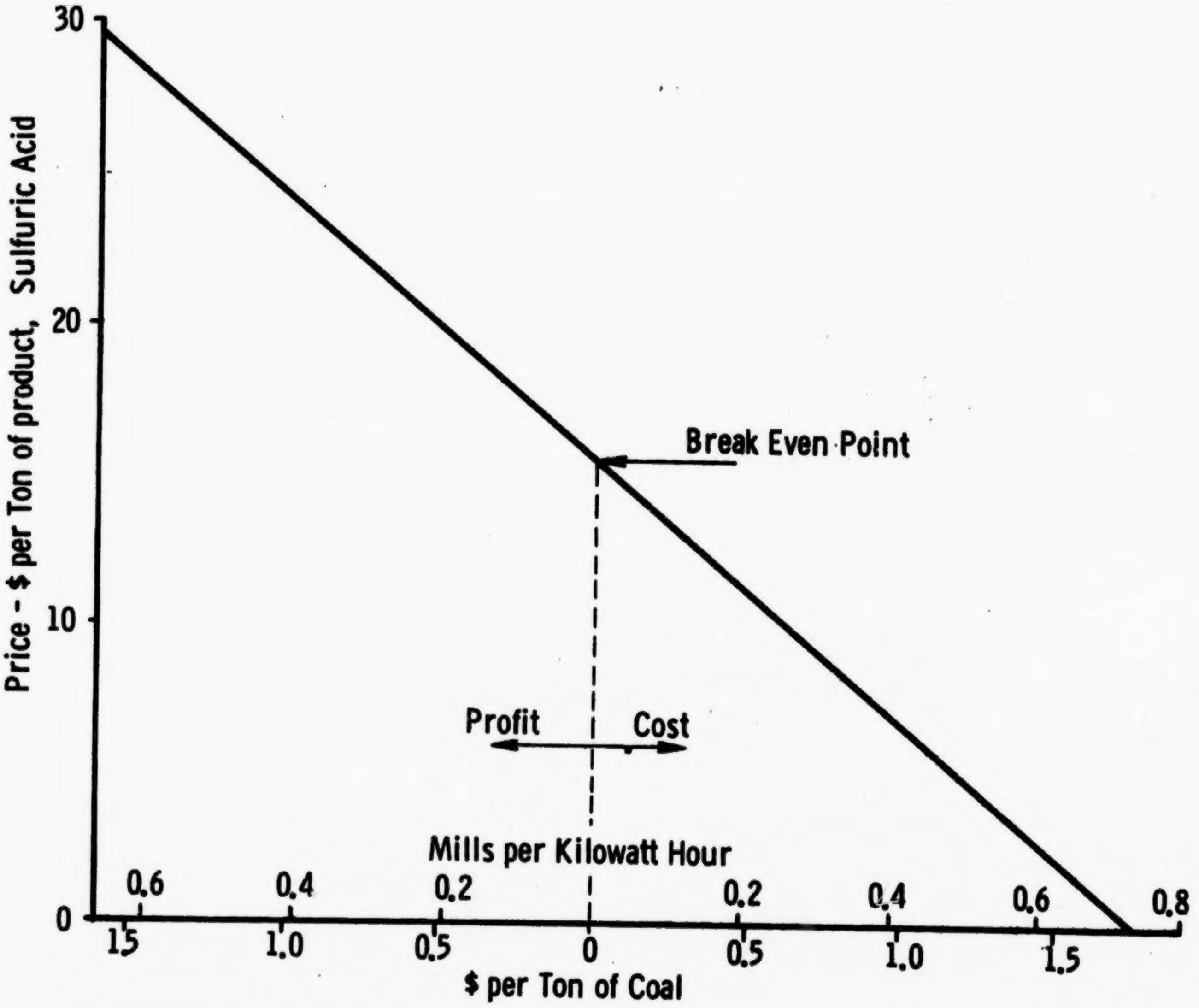


Figure 38. Effect of Product Credit on Operating Cost of MRC/NAPCA Process (Large New Power Plant Facility)

Table 15

CAPITAL COST ESTIMATE SUMMARY

Category: NEW POWER PLANT (HIGH TEMPERATURE EFFLUENT)

Case #1

Name of Process: MRC-NAPCA Process Flue Gas Rate: 2.5 MMSCFM

MW 1,400

		Cost - $	% of Total
1.	Purchased Equipment	6,632,000	19.15
2.	Purchased Equipment Installation	2,539,000	7.33
3.	Piping	2,653,000	7.66
4.	Instruments	995,000	2.87
5.	Insulation	800,000	2.30
6.	Electrical	663,000	1.91
7.	Building	663,000	1.91
8.	Land & Yard Improvements	995,000	2.87
9.	Utilities	995,000	2.87
10.	Incremental Cost of Precipitator	1,500,000	4.34
11.	Acid Tower Packing	455,000	1.31
12.	Mist Elements	2,340,000	6.76
13.	Initial Catalyst Cost	630,000	1.82
14.	Physical-Plant Cost	21,860,000	63.10
15.	Engineering and Construction	4,372,000	12.62
16.	Direct Plant Cost	26,232,000	75.72
17.	Contingency & Contractor's Fee	5,246,400	15.15
18.	Fixed Capital Cost	31,478,400	90.87
19.	Capitalized Cost of Catalyst	2,140,000	6.18
20.	Working Capital	1,021,000	2.95
	TOTAL INVESTMENT	34,639,400	100.00

21. Capital Requirements
$/KW Capacity 24.74

Table 16

EQUIPMENT COST ESTIMATE SUMMARY

Category: NEW POWER PLANT (HIGH TEMPERATURE EFFLUENT)

Name of Process: MRC-NAPCA Process Flue Gas Rate: 2.5 MMSCFM

MW 1400

Item	No. of Units	Cost - $
1. Catalytic Converters	4	792,000
2. Acid Towers & Mist Eliminators	8	2,080,000
3. Acid Coolers	8	2,780,000
4. Acid Pumps	8	64,000
5. I.D. Fans	8	720,000
6. Storage Tanks	2	196,000
Purchased Equipment Cost		6,632,000

Table 17

WORKING CAPITAL ESTIMATE SUMMARY

Category: NEW POWER PLANT (HIGH TEMPERATURE EFFLUENT)

Name of Process: MRC-NAPCA Process Flue Gas Rate: 2.5 MMSCFM

MW: 1400

Item	Cost - $	Percent
1. Raw material inventory, 1 Month	13,200	1.30
2. Direct labor, 3 Months	217,000	21.25
3. Indirect cost, 3 Months	235,600	23.08
4. Operating supplies, 3 Months	55,600	5.44
5. Fixed costs	222,300	21.78
6. Spare parts	185,300	18.14
7. Miscellaneous	92,000	9.01
TOTAL	1,021,000	100.00

Table 18

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @ 100% Capacity

Category: NEW POWER PLANT (HIGH TEMPERATURE EFFLUENT)

Name of Process MRC-NAPCA Process Flue Gas Rate 2.5 MMSCFM

MW 1,400

Fixed Capital Cost 31,478,400

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	249,000	3.05
2.	Direct Labor	105,000	1.28
3.	Supervision	23,400	0.28
4.	Maintenance, 5% of Fixed Capital	1,573,900	19.27
5.	Supplies, 15% of Maintenance	236,090	2.89
6.	Utilities	895,700	10.97
7.	Other	-	-
8.	TOTAL DIRECT COST	3,083,090	37.74
9.	Payroll Burden, 20% of 2 & 3	25,700	0.31
10.	Plant Overhead, 50% of 2, 3, 4 and 5	969,200	11.86
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	994,900	12.17
15.	Depreciation, 10 % Fixed Capital/Yr.	3,147,840	38.53
16.	Taxes, 2% of Fixed Capital	629,570	7.71
17.	Insurance, 1% of Fixed Capital	314,780	3.85
18.	Other	-	-
19.	TOTAL FIXED COST	4,092,190	50.09
20.	TOTAL OPERATING COST	8,170,180	100.00
21.	COST: $/Ton of Coal 1.78 Mill/kwh 0.737		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal ________ Mill/kwh ________		

The desorbed sulfur trioxide is fed to an absorption tower essentially the same as that in a contact sulfuric acid plant, to make 100% sulfuric acid and oleum.

As shown in the flow diagram in Figure 39, flue gas at high temperature (850° to 900°F) flows through a catalytic converter where 90% of the sulfur dioxide is converted to sulfur trioxide. Next it passes through an absorber-stripper where SO_3 is absorbed on a dry medium consisting of porous silica or alumina granules impregnated with 20% sodium sulfate. Sulfur trioxide is stripped from exhausted sorbent with hot gas from a furnace at 1000°F. The absorber-stripper is a fixed bed contactor designed very much like the converter to minimize pressure drop through the absorbent beds. Assuming the absorbent requirement is the stoichiometric amount, each absorber-stripper contains 13 bed sections in parallel and is 30 ft. in diameter by 117 ft. in height.

Four absorption towers are required to permit adequate cycle timing. This is illustrated by the following table:

ABSORBER NUMBER			
1	2	3	4
15 min abs.	---	---	---
15 min des.	15 min abs.	---	---
15 min des.	15 min des.	15 min abs.	---
15 min cool	15 min des.	15 min des.	15 min abs.

Clean, hot gases emerging during the absorption cycle, at about 820°F, are passed through an economizer and an air heater where heat is recovered for utilization in the power plant. An induced draft fan moves the clean gas through the system and up the stack.

The hot gas emerging during the desorption cycle is cooled to about 500°F in a gas cooler. Lower temperature would result in premature condensation of acid. The cooled gas is then directed to an acid recovery unit for producing concentrated acid. The sulfur trioxide concentration in this gas stream is high, as shown by the material balance in Table 19. Thus, the primary function of the acid tower, in this case, is absorption of SO_3 into 96-98% sulfuric acid. Mist eliminators are, again, required on the tail gas from the absorber. The interesting point is that the gas rate to the absorber is two orders of magnitude less than the main gas stream flow. Consequently, only a single acid tower is required compared to eight in Case I.

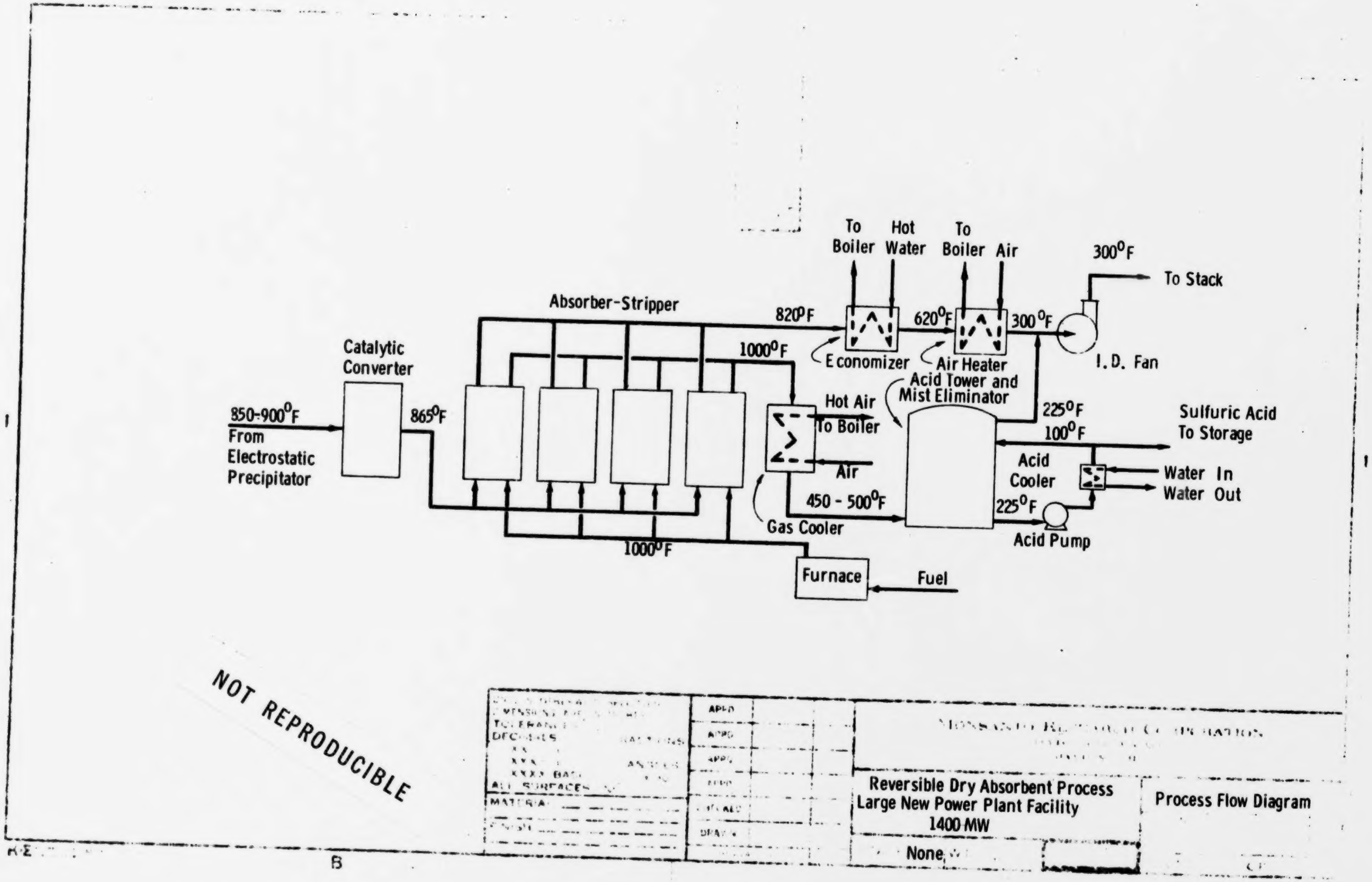

850-900°F
From
Electrostatic
Precipitator
Catalytic
Converter
865°F
Absorber-Stripper
1000°F
820°F
To
Boiler
Hot
Water
Economizer
620°F
To
Boiler
Air
Air Heater
300°F
300°F
To Stack
I. D. Fan
1000°F
Hot Air
To Boiler
Air
450 - 500°F
Gas Cooler
Acid Tower and
Mist Eliminator
225°F
100°F
Sulfuric Acid
To Storage
Acid
Cooler
Water In
Water Out
225°F
Acid Pump
1000°F
Furnace
Fuel
NOT REPRODUCIBLE
Reversible Dry Absorbent Process
Large New Power Plant Facility
1400 MW
Process Flow Diagram
None

Figure 39. Reversible Dry Absorbent Process, Process Flow Diagram

Table 19

SO_2 REMOVAL FROM FLUE GAS

CATEGORY: Large New Power Plant Facility

PROCESS FLOW SHEET

NAME OF PROCESS: Reversible Dry Absorbent

MW: 1400

FLUE GAS RATE: 2.5×10^6 SCFM

Process Stream	Flow			Temp.	Composition in Weight Percent							
	lb/hr	GPM	SCFM	°F	N_2	CO_2	H_2O	O_2	SO_2	NO_x	SO_3	H_2SO_4
from electrostatic precipitator to catalytic converter	11.81×10^6	---	2.50×10^6	850-900	70.27	21.66	4.37	3.00	0.64	0.05	---	---
from catalytic converter to absorber-stripper	11.81×10^6	---	2.50×10^6	865	70.18	21.64	4.40	2.93	0.06	0.06	0.73	---
from absorber-stripper to economizer	11.73×10^6	---	2.49×10^6	820	70.69	21.79	4.45	2.96	0.06	0.06	Trace	---
from furnace to absorber-stripper	0.118×10^6	---	2.5×10^4	1000	70.18	21.64	4.40	3.07	0.65	0.06	---	---
from absorber-stripper to gas cooler	0.199×10^6	---	3.1×10^4	1000	41.60	12.82	2.61	1.82	0.38	0.03	40.74	---
from gas cooler to acid tower and mist eliminator	0.199×10^6	---	3.1×10^4	450-500	41.60	12.82	2.61	1.82	0.38	0.03	40.74	---
from acid tower and mist eliminator to I.D. fan	0.118×10^6	---	2.5×10^4	225	70.19	21.64	4.40	3.08	0.64	0.05	Trace	---
from economizer to air heater	11.73×10^6	---	2.49×10^6	620	70.69	21.79	4.45	2.96	0.06	0.06	Trace	---
from air heater to I.D. fan	11.73×10^6	---	2.49×10^6	300	70.69	21.79	4.45	2.96	0.06	0.06	Trace	---
from I.D. fan to stack	11.847×10^6	---	2.5×10^6	300	70.69	21.79	4.45	2.95	0.07	0.05	Trace	---
from acid tower to storage	0.1×10^6	107.4	---	100	---	---	0.5	---	---	---	---	99.5

This difference is reflected in the comparative economics of cases I and I-A. Case I-A still requires four converters, but only one acid tower.

Additional assumptions employed in the cost estimates for Case I-A are:

• Absorption Efficiency	a) 100%, i.e., stoichiometric, for 15 minutes b) 50% stoichiometric for 15 minutes
• Desorption Efficiency	100% in 30 minutes
• Amount of Na_2SO_4 in total absorbent	20% (by weight)
• Cost of Absorbent	5¢/lb
• Absorbent Make-Up	0.1% of feed
• Cost of Coal	$4.00/ton

Capital and operating cost estimates are presented in Tables 20 through 23. The effect of product credit on net operating cost is shown in Figure 40.

D. Case II - MRC/NAPCA Process - Existing 220 Mw Plant

In this case, there is, in addition to a difference in size from Case I, the necessity to preheat the gas fed to the converter. (Figure 41) Except for these two points the process is the same as Case I. Because of the size difference only two converters, 30 ft. in diameter by 90 ft. in height, and two acid towers, 26 ft. in diameter by 54 ft. in height, are required. Each of the converters has ten catalyst beds in parallel.

In order to bring the flue gas to converter operating temperature, an auxiliary furnace is required. The main gas stream is heated by direct mixture with hot gas from the auxiliary burner. Figure 41 shows a flow diagram for one of the two trains needed for the 220 Mw, existing station. The flue gas heat exchanger and the auxiliary furnace handle the entire gas stream. Then, the stream splits to two conversion-recovery trains.

Table 24 shows the material balance for the treatment process. Capital and operating cost estimates are summarized in Tables 25 through 28. Figure 4[illegible] shows the effect of product credit on net operating cost.

Table 20

CAPITAL COST ESTIMATE SUMMARY

Category: NEW POWER PLANT (HIGH TEMPERATURE EFFLUENT)

Case #1A

Name of Process: Reversible Dry Absorbent Flue Gas Rate: 2.5 MMSCFM

MW 1400

		Cost - $	% of Total
1.	Purchased Equipment	2,934,000	16.79
2.	Purchased Equipment Installation	1,400,000	8.01
3.	Piping	1,470,000	8.41
4.	Instruments	440,000	2.52
5.	Insulation	353,000	2.02
6.	Electrical	294,000	1.68
7.	Building	294,000	1.68
8.	Land & Yard Improvements	440,000	2.52
9.	Utilities	440,000	2.52
10.	Incremental Cost of Precipitator	1,500,000	8.59
11.	Acid Tower Packing	30,000	0.17
12.	Mist Elements	---	---
13.	Initial Catalyst Cost	668,000	3.82
14.	Physical-Plant Cost	10,263,000	58.75
15.	Engineering and Construction	2,053,000	11.75
16.	Direct Plant Cost	12,316,000	70.50
17.	Contingency & Contractor's Fee	2,463,000	14.10
18.	Fixed Capital Cost	14,779,000	84.60
19.	Capitalized Cost of Catalyst	2,140,000	12.25
20.	Working Capital	551,000	3.15
	TOTAL INVESTMENT	17,470,000	100.00

21. Capital Requirements
$/KW Capacity 12.48

Table 21

EQUIPMENT COST ESTIMATE SUMMARY

Category: NEW POWER PLANT (HIGH TEMPERATURE EFFLUENT)

Name of Process: Reversible Dry Absorbent Flue Gas Rate: 2.5 MMSCFM

MW 1400

Item	Cost - $
1. Catalytic Converters	792,000
2. Absorber-Strippers	792,000
3. Furnace	200,000
4. Gas Cooler	65,000
5. Absorber and Mist Eliminator	205,000
6. Acid Cooler	50,000
7. Regenerator Blower	70,000
8. I.D. Fans	610,000
9. Storage Tanks	150,000
PURCHASED EQUIPMENT COST	2,934,000

Table 22

WORKING CAPITAL ESTIMATE SUMMARY

Category: NEW POWER PLANT (HIGH TEMPERATURE EFFLUENT)

Name of Process: **Reversible Dry Absorbent** Flue Gas Rate: 2.5 MMSCFM

MW: 1400

Item	Cost, $	Percent
1. Raw Materials & Chemicals Inventory, 1 Month	70,000	12.71
2. Direct Labor, 3 Months	113,000	20.51
3. Indirect Cost, 3 Months	115,600	20.98
4. Operating Supplies, 3 Months	24,300	4.41
5. Fixed Costs	97,100	17.62
6. Spare Parts	81,000	14.70
7. Miscellaneous	50,000	9.07
TOTAL	551,000	100.00

Table 23

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @ 100% Capacity

Category: NEW POWER PLANT (HIGH TEMPERATURE EFFLUENT)

Name of Process: Reversible Dry Absorbent Flue Gas Rate: 2.5 MMSCFM

MW 1400

Fixed Capital Cost: $14,779,000

ITEM	TOTAL $	PER CENT
1. Raw Materials & Chemicals	731,000	15.26
2. Direct Labor	105,000	2.19
3. Supervision	23,400	0.49
4. Maintenance, 5% of Fixed Capital	739,000	15.43
5. Supplies, 15% of Maintenance	110,800	2.31
6. Utilities	645,000	13.46
7. Other	---	---
8. TOTAL DIRECT COST	2,354,200	49.15
9. Payroll Burden, 20% of 2 & 3	25,700	0.54
10. Plant Overhead, 50% of 2, 3, 4 and 5	489,100	10.21
11. Pack & Ship	---	---
12. Waste Disposal	---	---
13. Other	---	---
14. TOTAL INDIRECT COST	514,800	10.75
15. Depreciation, 10% Fixed Capital/Yr.	1,477,900	30.85
16. Taxes, 2% of Fixed Capital	295,600	6.17
17. Insurance, 1% of Fixed Capital	147,800	3.08
18. Other	---	---
19. TOTAL FIXED COST	1,921,300	40.11
20. TOTAL OPERATING COST	4,790,300	100.00
21. COST: $/Ton of Coal 1.043 Mill/kwh 0.432		
22. BY-PRODUCT CREDIT		
23. ADJUSTED OPERATING COST		
24. ADJUSTED COST: $/Ton of Coal ______ Mill/kwh ______		

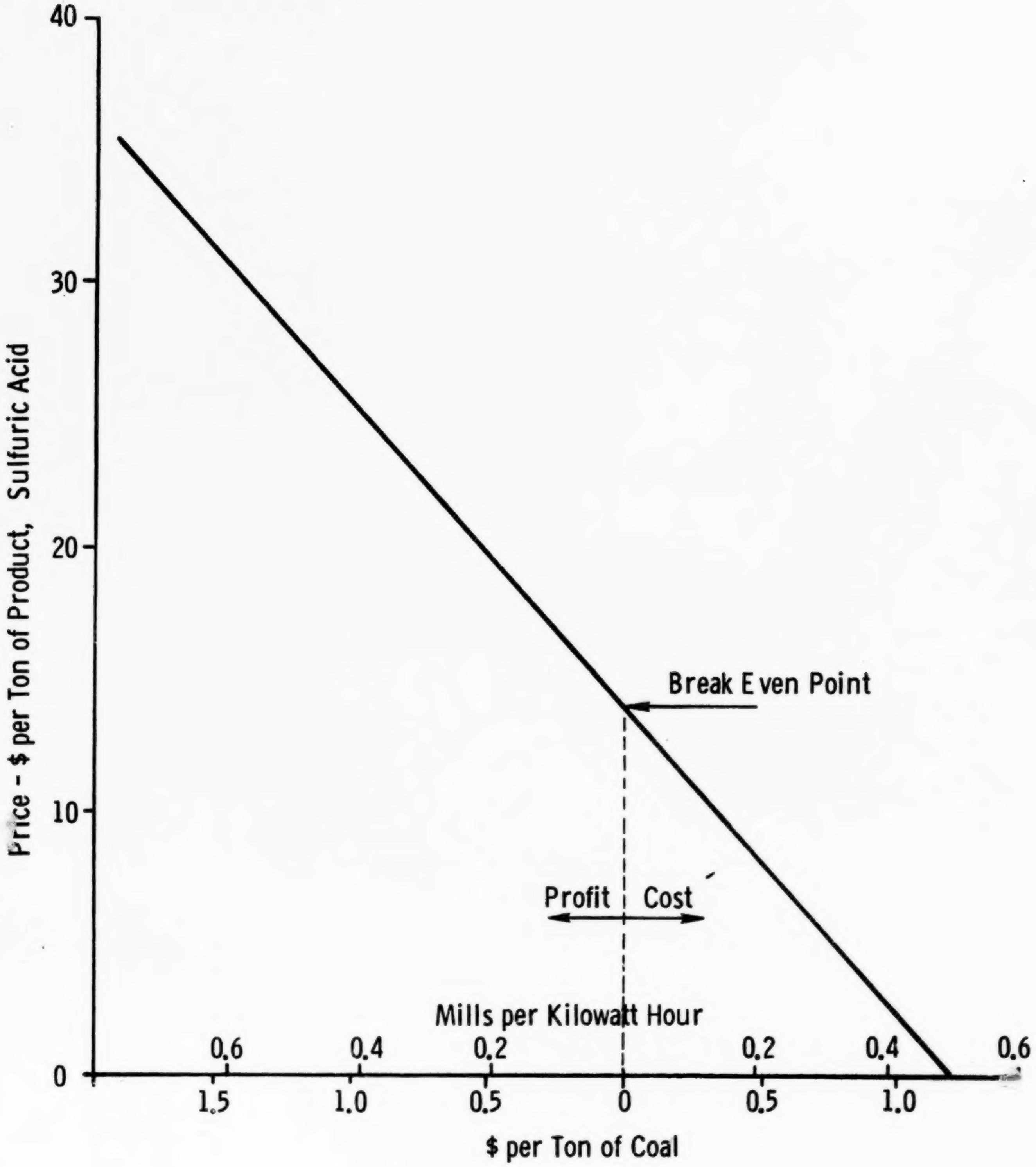


Figure 40. Effect of Product Credit on Operating Cost of Reversible Dry Absorbent Process (Large New Power Plant Facility)

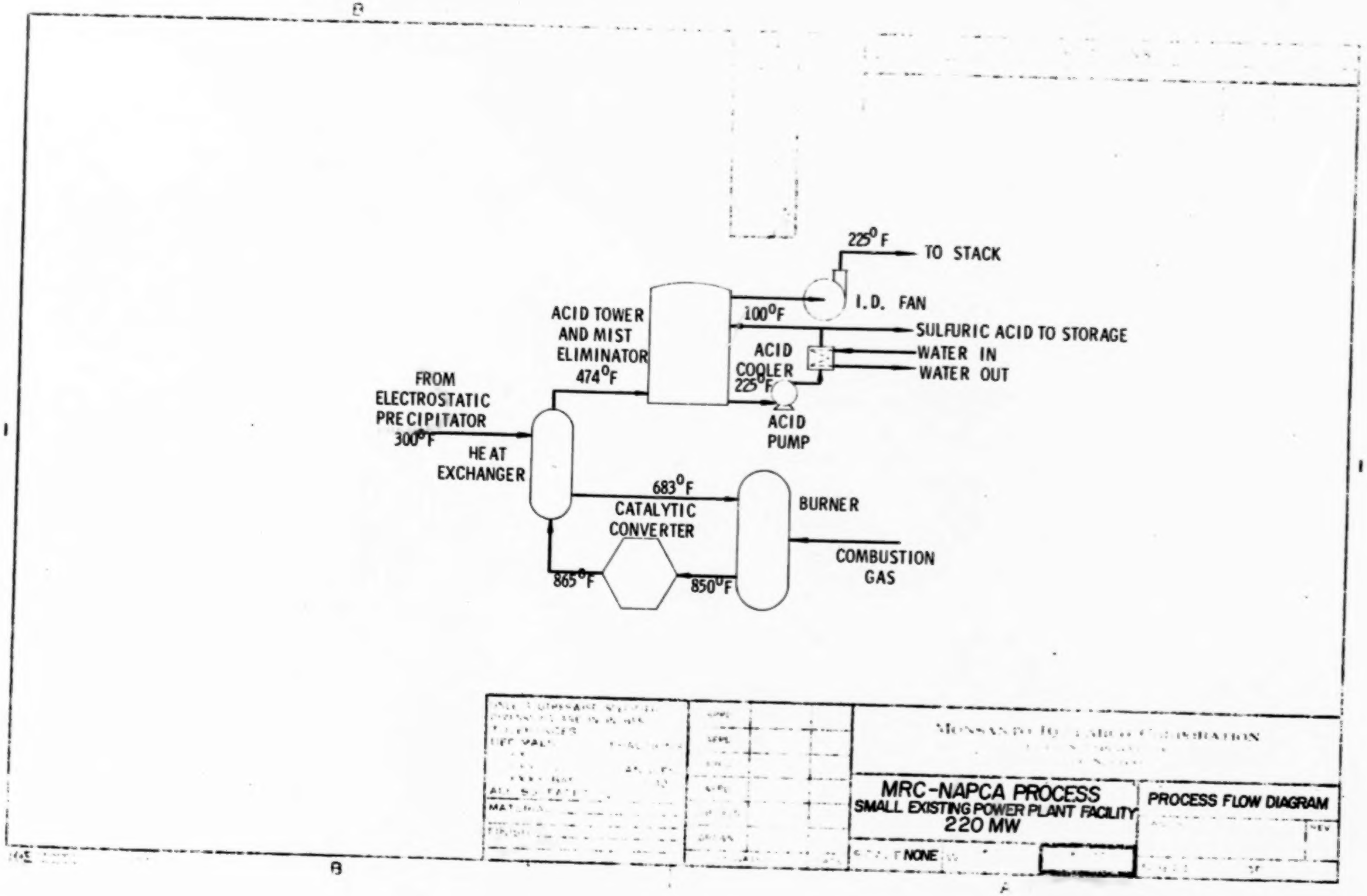

225°F
TO STACK
I.D. FAN
100°F
SULFURIC ACID TO STORAGE
WATER IN
WATER OUT
ACID COOLER
225°F
ACID PUMP
ACID TOWER AND MIST ELIMINATOR
474°F
FROM ELECTROSTATIC PRECIPITATOR
300°F
HEAT EXCHANGER
683°F
CATALYTIC CONVERTER
865°F
850°F
BURNER
COMBUSTION GAS
MRC-NAPCA PROCESS
SMALL EXISTING POWER PLANT FACILITY
220 MW
PROCESS FLOW DIAGRAM
NONE

Figure 41. MRC-NAPCA Process, Small Existing Power Plant Facility, 220 MW Process Flow Diagram

Table 24

SO_2 REMOVAL FROM FLUE GAS

CATEGORY: Small Existing Power Plant Facility

PROCESS FLOW SHEET

NAME OF PROCESS: MRC-NAPCA Process MW: 220 FLUE GAS RATE: 0.5 x 10^6 SCFM

Process Stream	Flow			Temp. °F	Composition in Weight Percent								
	lb/hr	GPM	SCFM		N_2	CO_2	H_2O	O_2	SO_2	NO_x	SO_3	H_2SO_4	CH_4
from boiler to flue gas heat exchanger	2.36x10^6	---	0.50x10^6	300	70.27	21.66	4.37	3.00	0.64	0.05	---	---	---
from flue gas heat exchanger to burner	2.36x10^6	---	0.50x10^6	683	70.27	21.66	4.37	3.00	0.64	0.05	---	---	---
from burner to catalytic converter	2.58x10^6	---	0.55x10^6	850	70.52	20.87	4.69	3.08	0.59	0.05	---	---	---
from catalytic converter to flue gas heat exchanger	2.58x10^6	---	0.55x10^6	865	70.52	20.87	4.74	2.95	0.06	0.05	0.03	0.77	---
from flue gas heat exchanger to acid tower	2.58x10^6	---	0.55x10^6	474	70.52	20.87	4.74	2.95	0.06	0.05	0.03	0.77	---
from acid tower to stack	2.56x10^6	---	0.55x10^6	225	71.25	21.09	4.53	2.98	Trace	0.05	Trace	Trace	---
combustion gas to burner	0.22x10^6	---	0.05x10^6	---	73.20	---	---	22.22	---	---	---	---	4.58
product acid to storage	26.5x10^3	39.13	---	100	---	---	25.00	---	---	---	---	75.00	---

Table 25

CAPITAL COST ESTIMATE SUMMARY

Category: SMALL EXISTING POWER PLANT

Case #2

Name of Process: MRC-NAPCA Process Flue Gas Rate: 0.5 MMSCFM

MW 220

		Cost - $	% of Total
1.	Purchased Equipment	2,014,000	19.73
2.	Purchased Equipment Installation	770,500	7.55
3.	Piping	1,007,000	9.87
4.	Instruments	302,100	2.95
5.	Insulation	241,700	2.37
6.	Electrical	201,400	1.98
7.	Building	201,400	1.98
8.	Land & Yard Improvements	302,100	2.95
9.	Utilities	302,100	2.95
10.	Incremental Cost of Precipitator	500,000	4.89
11.	Acid Tower Packing	54,000	0.52
12.	Mist Elements	520,000	5.09
13.	Initial Catalyst Cost	126,400	1.23
14.	Physical-Plant Cost	6,542,700	64.06
15.	Engineering and Construction	1,308,600	12.81
16.	Direct Plant Cost	7,851,300	76.87
17.	Contingency & Contractor's Fee	1,570,300	15.38
18.	Fixed Capital Cost	9,421,600	92.25
19.	Capitalized Cost of Catalyst	426,000	4.18
20.	Working Capital	365,200	3.57
	TOTAL INVESTMENT	10,212,800	100.00

21. Capital Requirements

$/KW Capacity 46.42

Table 26

EQUIPMENT COST ESTIMATE SUMMARY

Category: SMALL EXISTING POWER PLANT

Name of Process: MRC-NAPCA Process Flue Gas Rate: 0.5 MMSCFM

MW 220

Item	Cost - $
Catalytic Converter	278,000
Acid Tower & Mist Eliminator	340,000
Acid Cooler	540,000
Acid Pump	12,500
Flue Gas Heat Exchanger	595,000
I. D. Fan	180,000
Flue Gas Burner	8,500
Storage Tank	60,000
Purchased Equipment Cost	2,014,000

Table 27

WORKING CAPITAL ESTIMATE SUMMARY

Category: SMALL EXISTING POWER PLANT

Name of Process: MRC-NAPCA Process Flue Gas Rate: 0.5 MMSCFM

MW 220

Item	Cost - $	Percent
1. Raw Material Inventory 1 Month	36,200	9.92
2. Direct Labor, 3 Months	78,600	21.52
3. Indirect Cost, 3 Months	79,700	21.82
4. Operating Supplies 3 Months	16,500	4.51
5. Fixed Costs	66,000	18.07
6. Spare Parts	55,000	15.06
7. Miscellaneous	33,200	9.10
Total	365,200	100.00

Table 28

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @ 60% Capacity

Category: SMALL EXISTING POWER PLANT

Name of Process MRC-NAPCA Process Flue Gas Rate 0.5 MMSCFM

MW 220

Fixed Capital Cost 9,421,600

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	444,250	15.96
2.	Direct Labor	79,000	2.84
3.	Supervision	15,600	0.56
4.	Maintenance, 5% of Fixed Capital	471,080	16.93
5.	Supplies, 15% of Maintenance	70,700	2.53
6.	Utilities	141,000	5.07
7.	Other	-	-
8.	TOTAL DIRECT COST	1,221,630	43.89
9.	Payroll Burden, 20% of 2 & 3	18,920	0.67
10.	Plant Overhead, 50% of 2, 3, 4 and 5	318,190	11.44
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	337,110	12.11
15.	Depreciation, 10 % Fixed Capital/Yr.	942,160	33.85
16.	Taxes, 2% of Fixed Capital	188,440	6.77
17.	Insurance, 1% of Fixed Capital	94,220	3.38
18.	Other	-	-
19.	TOTAL FIXED COST	1,224,820	44.00
20.	TOTAL OPERATING COST	2,783,560	100.00
21.	COST: $/Ton of Coal 6.51 Mill/kwh 2.66		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal ____ Mill/kwh ____		

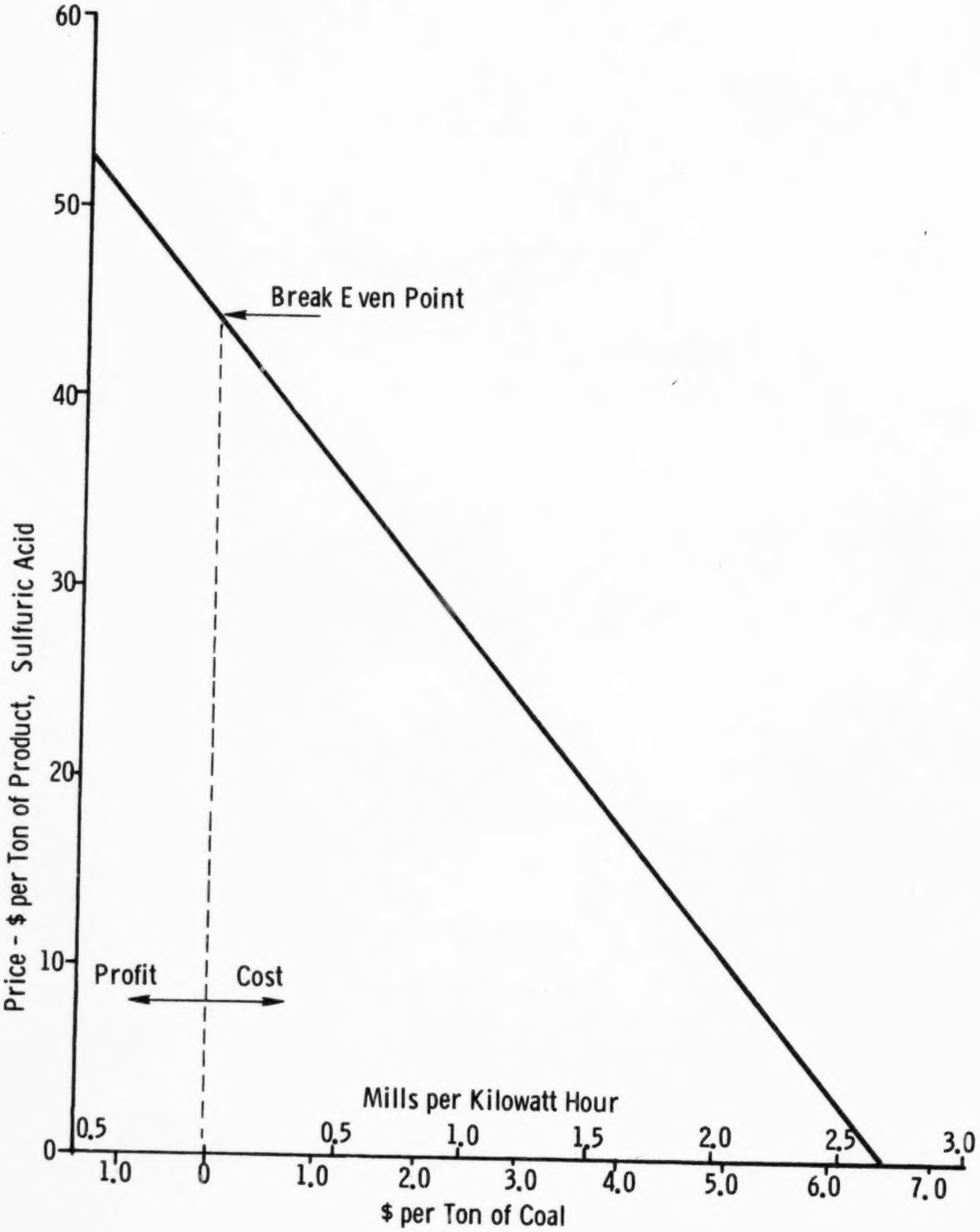


Figure 42. Effect of Product Credit on Operating Cost of MRC-NAPCA Process (Small Existing Power Plant Facility)

Additional assumptions employed in material balance and cost estimates for Case II are:

• Flue Gas Rate	0.5 MM SCFM
• Size of Power Plant	220 Mw
• Coal Required for Power Plant	90 tons/hr
• Operating Factor	330 days/year @ 60% capacity
• SO_2 Conversion	90%
• SO_3 Recovered as H_2SO_4	95%
• Flue Gas Temperature	300°F
• Cost of 3" Intalox Saddles	$4.55/ft^3
• Cost of Natural Gas	35¢/1000 CF

E. Case III - Small Copper Smelter

For this case, the basic process was applied to the off-gas from the reverberatory furnace at a small copper smelter facility. Data used in the design were obtained from a derived model of a copper plant (Ref. 1). In examining this model it appears that, of two sulfur dioxide laden off-gas streams, that from the reverberatory furnace is the appropriate one for the type of process described in this report. Sulfur dioxide concentrations in the two streams, i.e., reverberatory furnace and matte converter, are 1.45 vol % and 3.82 vol %, respectively. An interesting question arises. It is obvious that the basic MRC/NAPCA process is a modification of "standard practice" contact sulfuric acid production. The question is: What is the dividing line? It is generally thought that the lower limit, or "breakeven" point for "standard" contact plant operation is about 3% SO_2 in the converter feed. On this basis, then, we would assign to the MRC/NAPCA type process, those gas streams containing less than 3 vol % SO_2. Thus, the present design for a smelter was limited to the reverberatory furnace off-gas.

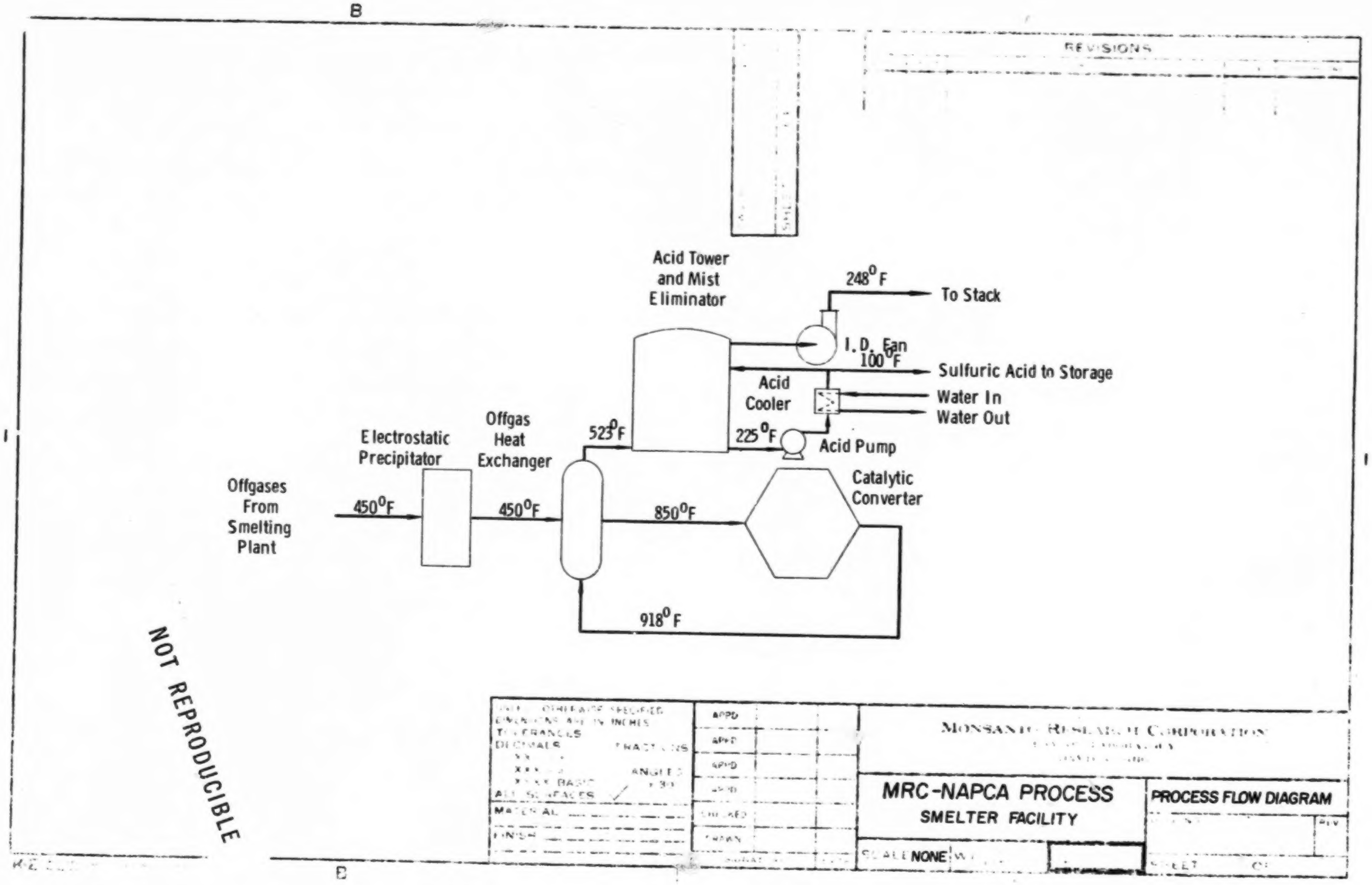
Figure 43 shows a schematic flow diagram for the process. The material balance is shown in Table 29. Again, because of the greatly reduced size compared with a 1400 Mw power plant, the smelter facility requires only one converter, 30 ft. in diameter by 80 ft.

in height, and one acid tower, 20 ft. in diameter by 46 ft. in height. The converter consists of nine catalyst beds in parallel.

For this case, the pertinent assumptions, over and above the general ones cited earlier, are as follows:

Off-Gas Rate	90,800 SCFM
Copper Production Capacity	230 tons/day
Operating Factor	330 days/year @ 100% capacity
SO_2 Conversion	90%
SO_3 Recovered as H_2SO_4	95%
Off-Gas Temperature	450°F
Cost of 3" Intalox Saddles	$\$4.55/ft^3$

Here, as in all previous cases, the amount of vanadia catalyst is derived from Figure 32. Tables 30 through 33 show capital and operating cost estimates and Figure 44 shows the effect of product sale price on net operating cost.


B
REVISIONS
Acid Tower
and Mist
Eliminator
248⁰ F
To Stack
I. D. Fan
100⁰F
Sulfuric Acid to Storage
Acid
Cooler
Water In
Water Out
Offgas
Heat
Exchanger
Electrostatic
Precipitator
523⁰F
225 ⁰F
Acid Pump
Catalytic
Converter
Offgases
From
Smelting
Plant
450⁰F
450⁰F
850⁰F
918⁰ F
MONSANTO RESEARCH CORPORATION
MRC-NAPCA PROCESS
SMELTER FACILITY
PROCESS FLOW DIAGRAM
SCALE NONE
B

NOT REPRODUCIBLE

Figure 43. MRC-NAPCA Process, Smelter Facility

Table 29

SO_2 REMOVAL FROM FLUE GAS

CATEGORY: Smelter Facility

PROCESS FLOW SHEET

NAME OF PROCESS: MRC-NAPCA Process

FLUE GAS RATE: 90,800 SCFM

Process Stream	Flow			Temp.	Composition in Weight Percent								
	lb/hr	GPM	SCFM	°F	N_2	CO_2	H_2O	O_2	SO_2	NO_x	SO_3	H_2SO_4	CH_4
from smelting plant to electrostatic precipitator	0.43×10^6	---	90,800	450	75.25	5.36	5.64	10.50	3.25	---	---	---	---
from electrostatic precipitator to heat exchanger	0.43×10^6	---	90,800	450	75.25	5.36	5.64	10.50	3.25	---	---	---	---
from heat exchanger to converter	0.43×10^6	---	90,800	850	75.25	5.36	5.64	10.50	3.25	---	---	---	---
from converter to heat exchanger	0.43×10^6	---	89,081	918	75.25	5.36	4.85	9.77	Trace	---	Trace	4.25	---
from heat exchanger to acid tower	0.43×10^6	---	89,081	523	75.25	5.36	4.85	9.77	Trace	---	Trace	4.25	---
from acid tower to stack	0.41×10^6	---	85,913	248	79.77	5.68	3.64	10.36	Trace	---	Trace	Trace	---
product acid to storage	24,600	36.3	---	100	---	---	25.00	---	---	---	---	75.00	---

Table 30

CAPITAL COST ESTIMATE SUMMARY

Category: SMELTER FACILITY

Case # 3

Name of Process: MRC-NAPCA Process Off-gas Rate: 90,800 SCFM

		Cost - $	% of Total
1.	Purchased Equipment	1,306,000	20.50
2.	Purchased Equipment Installation	524,700	8.24
3.	Piping	653,000	10.25
4.	Instruments	195,900	3.08
5.	Insulation	156,800	2.46
6.	Electrical	130,600	2.04
7.	Building	130,600	2.04
8.	Land & Yard Improvements	195,900	3.08
9.	Utilities	195,900	3.08
10.	Incremental Cost of Precipitator	--	--
11.	Acid Tower Packing	12,000	0.18
12.	Mist Elements	226,000	3.55
13.	Initial Catalyst Cost	164,000	2.57
14.	Physical-Plant Cost	3,891,400	61.07
15.	Engineering and Construction	778,300	12.21
16.	Direct Plant Cost	4,669,700	73.28
17.	Contingency & Contractor's Fee	934,000	14.66
18.	Fixed Capital Cost	5,603,700	87.94
19.	Capitalized Cost of Catalyst	553,500	8.69
20.	Working Capital	214,730	3.37
	TOTAL INVESTMENT	6,371,930	100.00

Table 31

EQUIPMENT COST ESTIMATE SUMMARY

Category: SMELTER FACILITY

Name of Process: MRC-NAPCA Process Flue Gas Rate: 90,800 SCFM

Item	Cost -$
Electrostatic Precipitator	430,000
Catalytic Converter	143,000
Acid Tower & Mist Eliminator	320,000
Acid Cooler	96,000
Acid Pump	2,000
I.D. Fan	45,000
Off-gas Heat Exchanger	205,000
Storage Tank	65,000
Purchased Equipment Cost	1,306,000

Table 32

WORKING CAPITAL ESTIMATE SUMMARY

Category: SMELTER FACILITY

Name of Process: MRC-NAPCA Process Off Gas Rate: 90,800 SCFM

Item	Cost - $	Percent
1. Raw Material Inventory, 1 Month	3,420	1.60
2. Direct Labor, 3 Months	52,050	24.24
3. Indirect Cost, 3 Months	52,200	24.30
4. Operating Supplies, 3 Months	10,500	4.88
5. Fixed Costs	42,030	19.58
6. Spare Parts	35,030	16.32
7. Miscellaneous	19,500	9.08
TOTAL	214,730	100.00

Table 33

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @ 100% Capacity

Category: SMELTER FACILITY

Name of Process MRC-NAPCA Process Off-gas Rate 90,800 SCFM

Fixed Capital Cost 5,603,700

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	41,000	2.96
2.	Direct Labor	52,500	3.79
3.	Supervision	15,600	1.12
4.	Maintenance, 5% of Fixed Capital	280,200	20.21
5.	Supplies, 15% of Maintenance	42,000	3.03
6.	Utilities	18,300	1.31
7.	Other	--	--
8.	TOTAL DIRECT COST	449,600	32.42
9.	Payroll Burden, 20% of 2 & 3	13,600	0.98
10.	Plant Overhead, 50% of 2, 3, 4 and 5	195,200	14.07
11.	Pack & Ship	--	--
12.	Waste Disposal	--	--
13.	Other	--	--
14.	TOTAL INDIRECT COST	208,800	15.05
15.	Depreciation, 10 % Fixed Capital/Yr.	560,400	40.41
16.	Taxes, 2% of Fixed Capital	112,100	8.09
17.	Insurance, 1% of Fixed Capital	56,000	4.03
18.	Other	--	--
19.	TOTAL FIXED COST	728,500	52.53
20.	TOTAL OPERATING COST	1,386,900	100.00

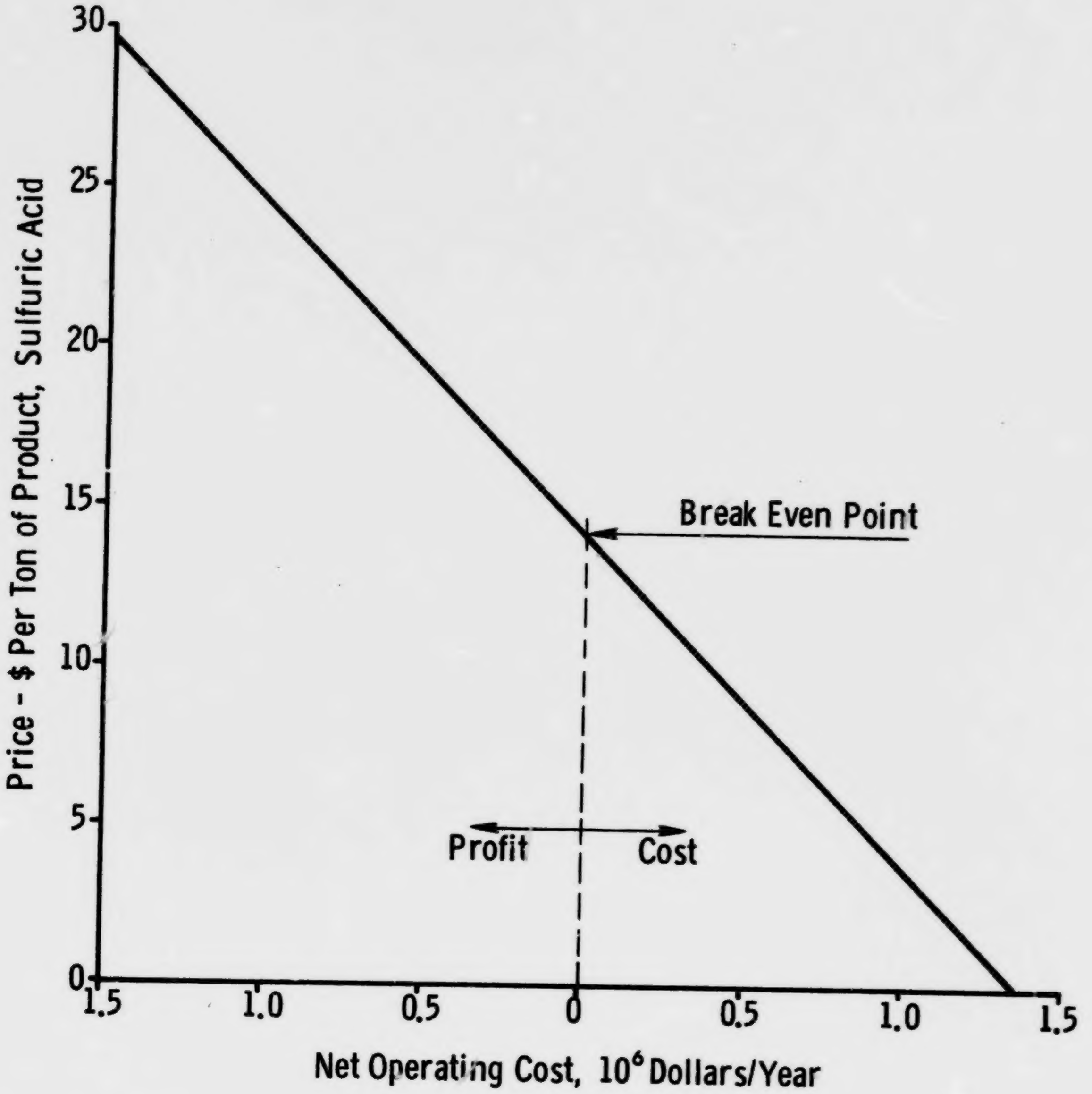


Figure 44. Effect of Product Credit on Operating Cost of MRC-NAPCA Process (Smelter Facility)

REFERENCES

1. Arthur G. McKee and Company, Systems Study for Control of Emissions - Primary Nonferrous Smelting Industry, Vol. III (Final Report), Contract PH 86-65-85, Plate No. C-1, San Francisco, June 1969.

APPENDIX I

COMMERCIAL CATALYST TEST DATA

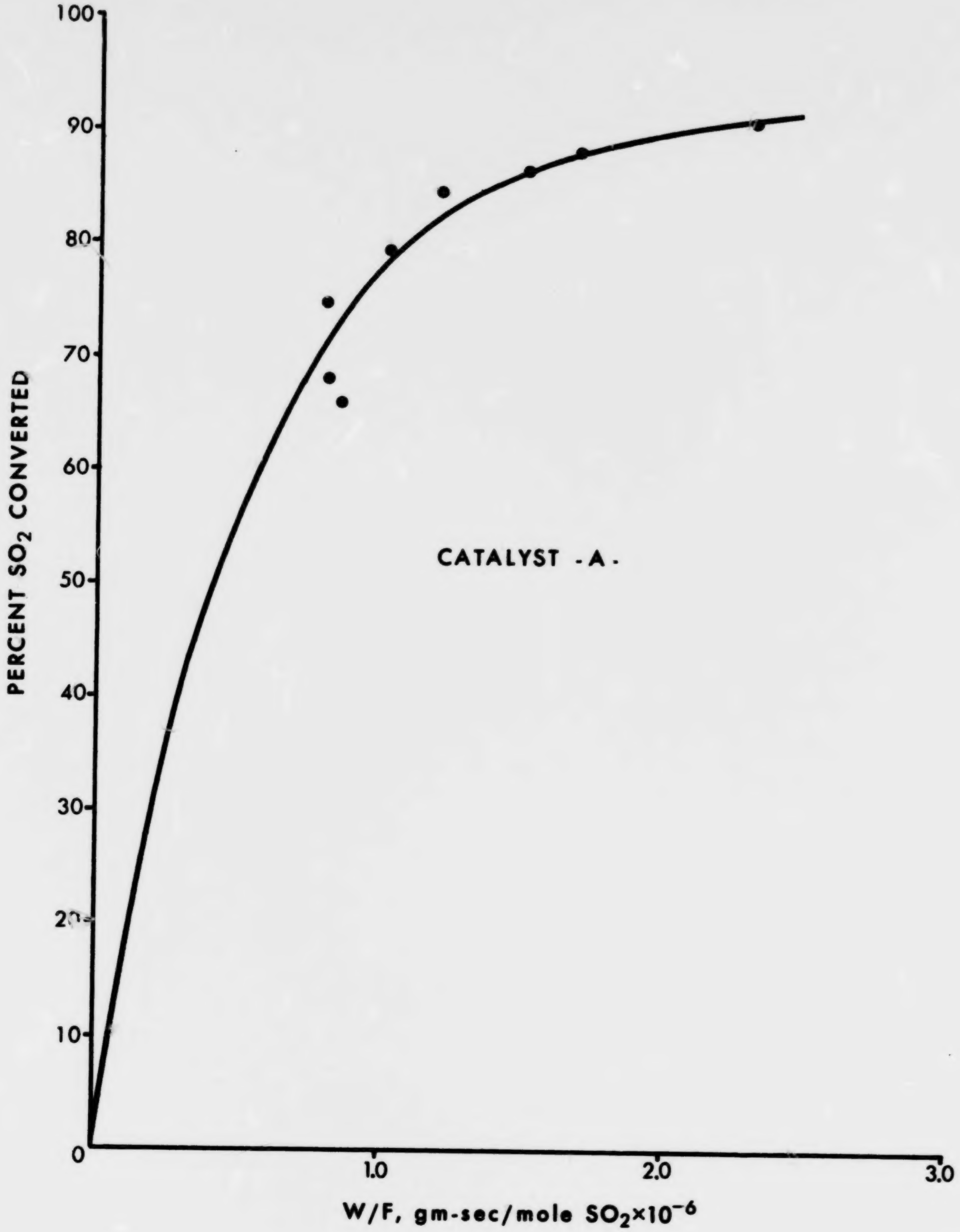


Figure 45. W/F-Conversion Profile for Catalyst 'A' at 900°F

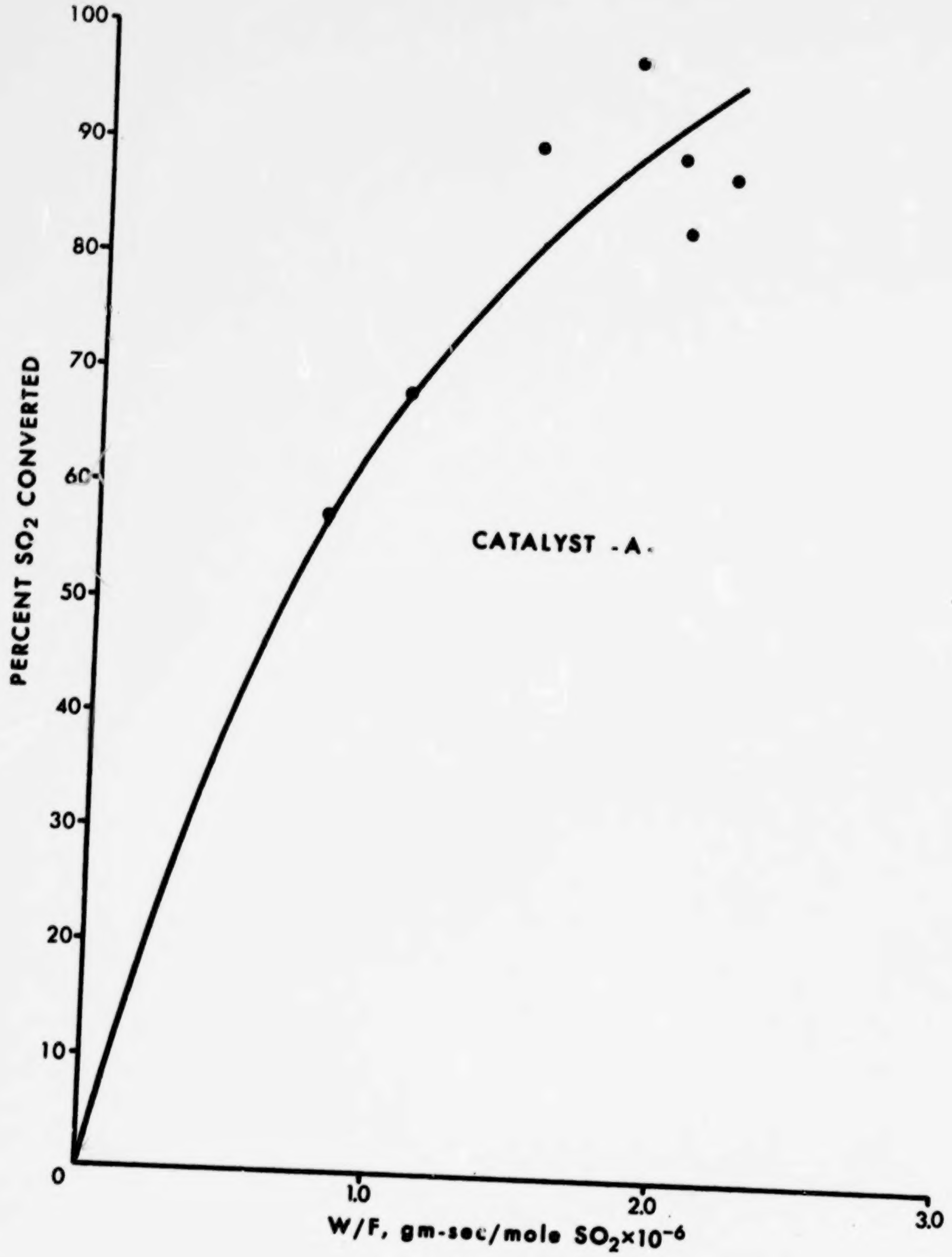


Figure 46. W/F-Conversion Profile for Catalyst 'A' at 850°F

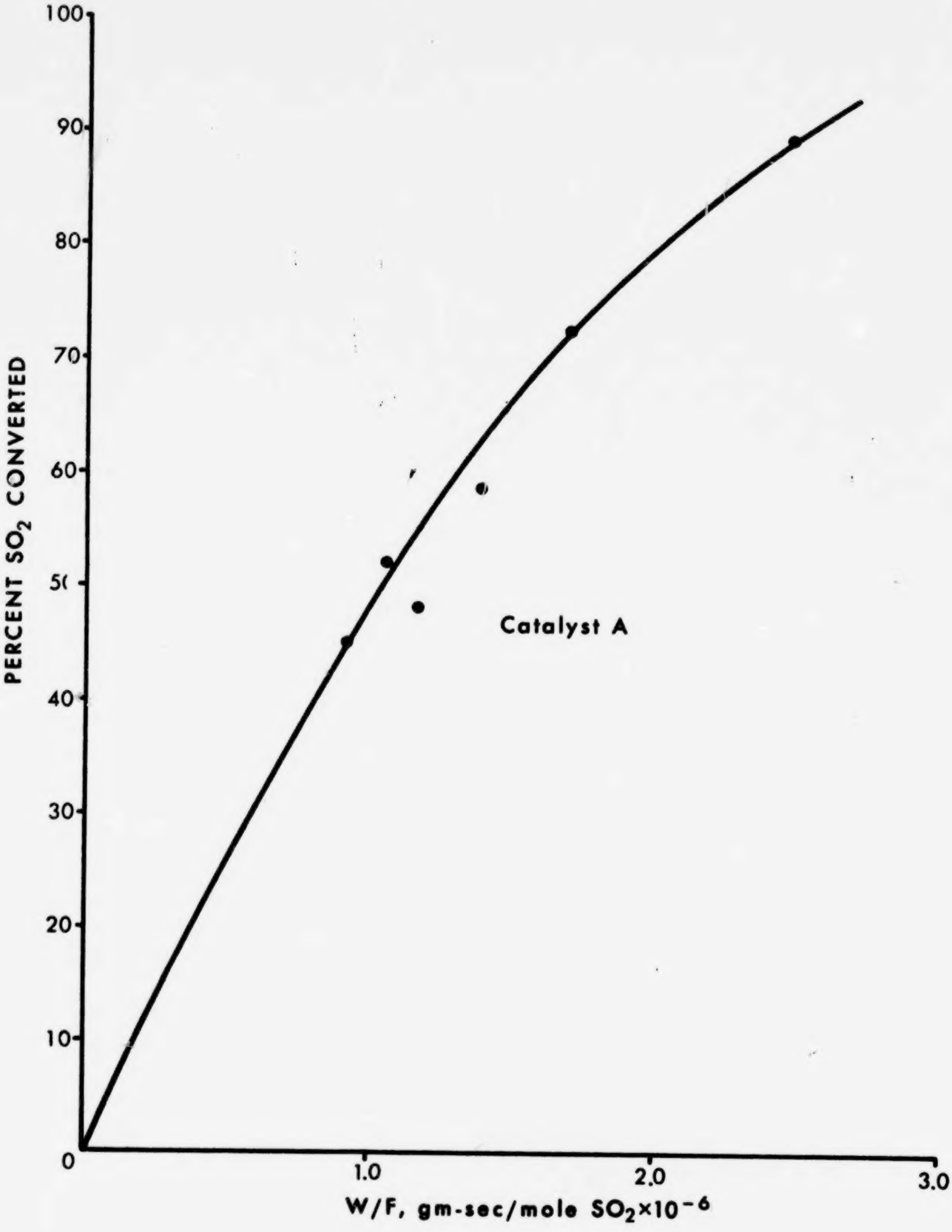


Figure 47. W/F-Conversion Profile for Catalyst 'A' at 800°F

Table 34

CATALYST - "A" TEST RESULTS

Run No.	% SO_2 in feed (mole)	Catalyst Weight (g)	Total Flow (cc/sec)	W/F (g-sec/cc)	W/F (g-sec/ mole SO_2)	Temp. (°F)	% Conversion
1	0.34	6.0	40	0.15	1.07	800	52
2	0.34	6.0	40	0.15	1.07	850	68
3	0.31	6.0	60	0.10	0.787	850	68
4	0.30	6.0	60	0.00	0.81	900	68
5	0.34	8.5	30	0.283	2.03	850	83
6	0.319	8.5	30	0.283	2.16	850	88
7	0.346	8.5	30	0.283	2.00	850	89
8	0.280	8.5	40	0.212	1.85	850	98
9	0.281	8.5	50	0.170	1.48	850	90
10	0.296	8.5	60	0.142	1.17	800	49
11	0.300	8.5	50	0.170	1.38	800	59
12	0.292	8.5	40	0.212	1.77	800	75
13	0.318	8.5	70	0.121	0.93	800	45
14	0.282	8.5	30	0.283	2.45	800	90
15	0.276	8.5	50	0.170	1.50	900	87
16	0.308	8.5	40	0.212	1.68	900	88
17	0.302	8.5	30	0.283	2.29	900	91
18	0.291	8.5	60	0.142	1.19	900	85
19	0.284	8.5	70	0.121	1.04	900	80
20	0.322	8.5	80	0.106	0.80	900	75

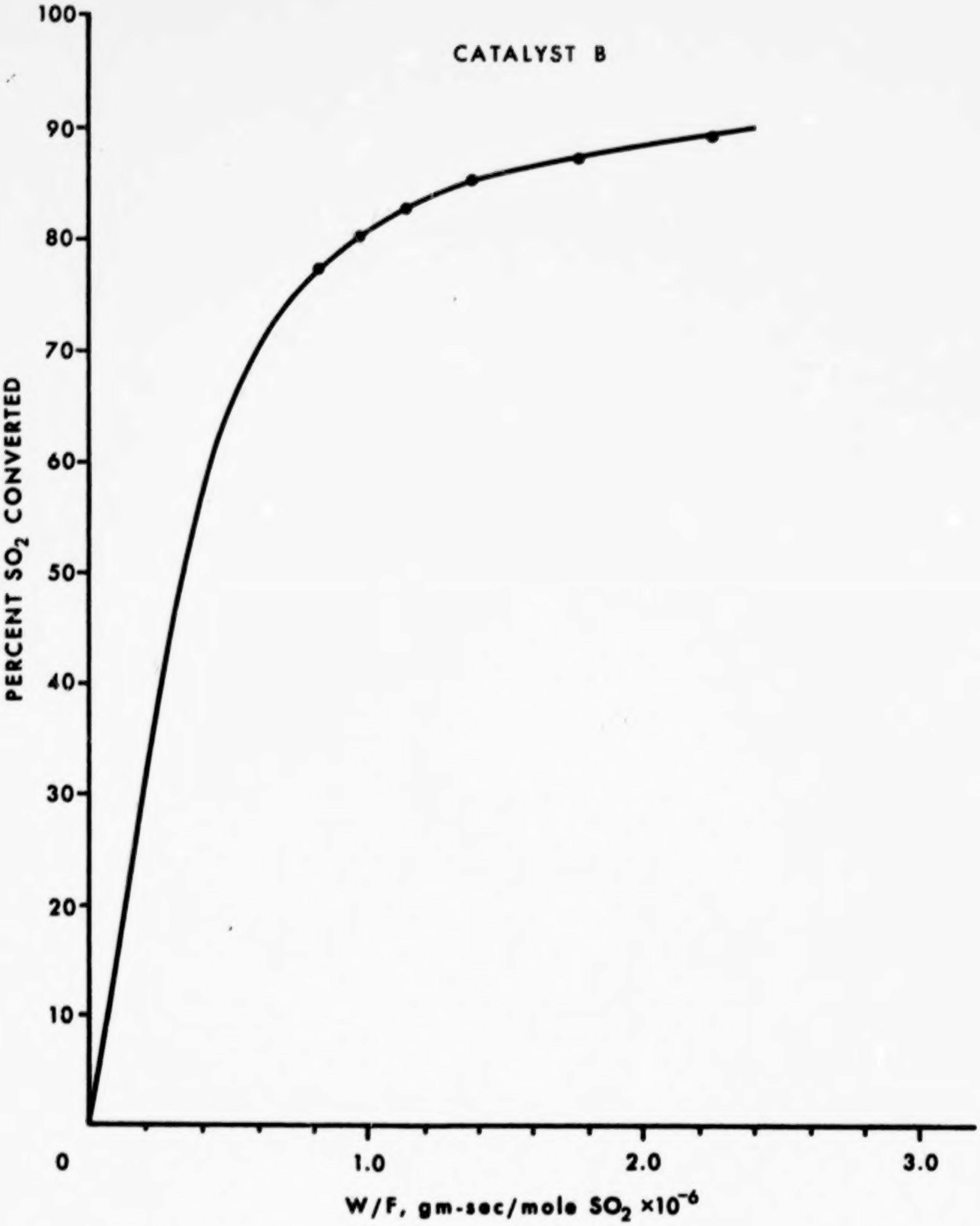


Figure 48. Effect of W/F on Conversion with Catalyst-B at 900°F

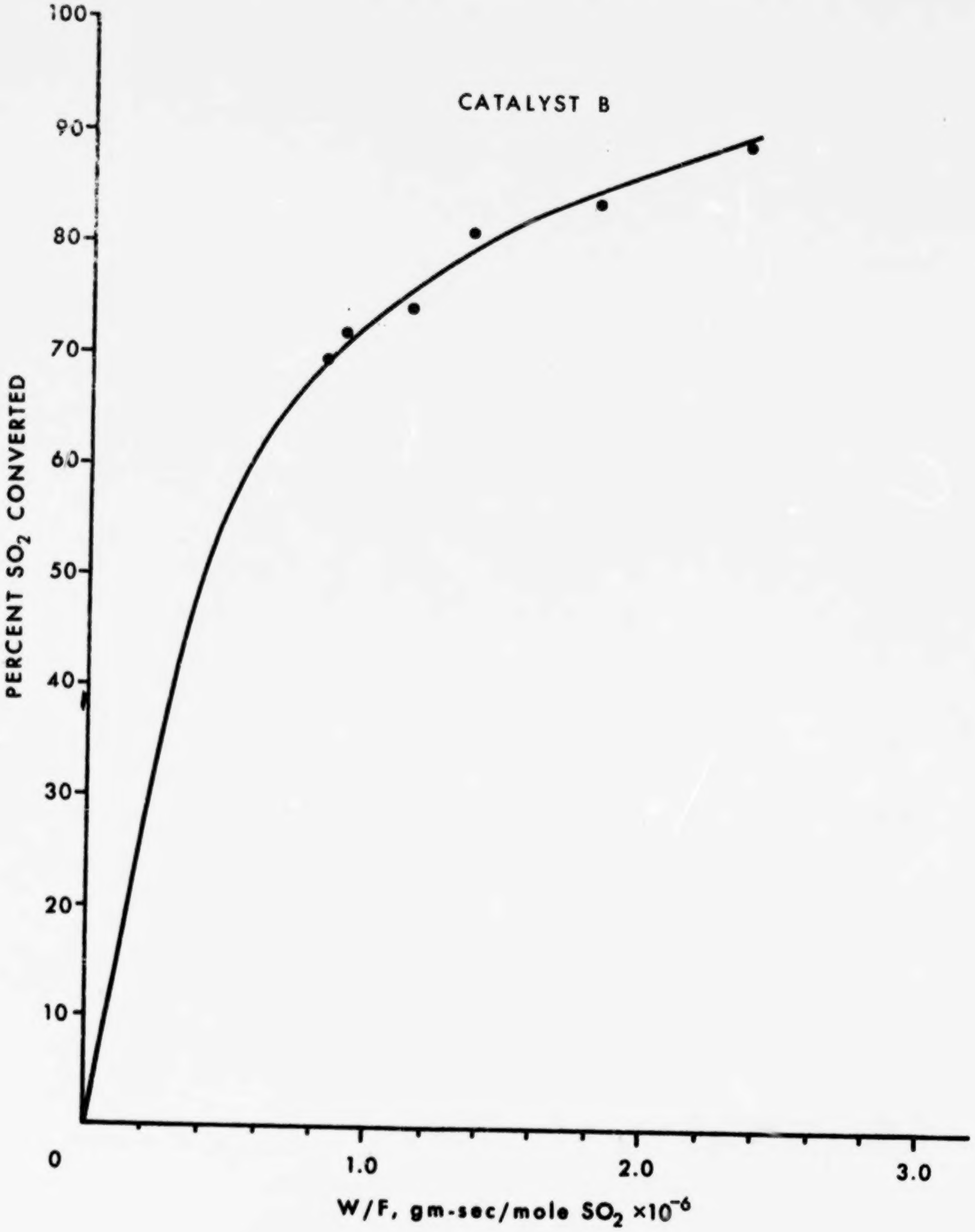


Figure 49. Effect of W/F on Conversion with Catalyst-B at 850°F

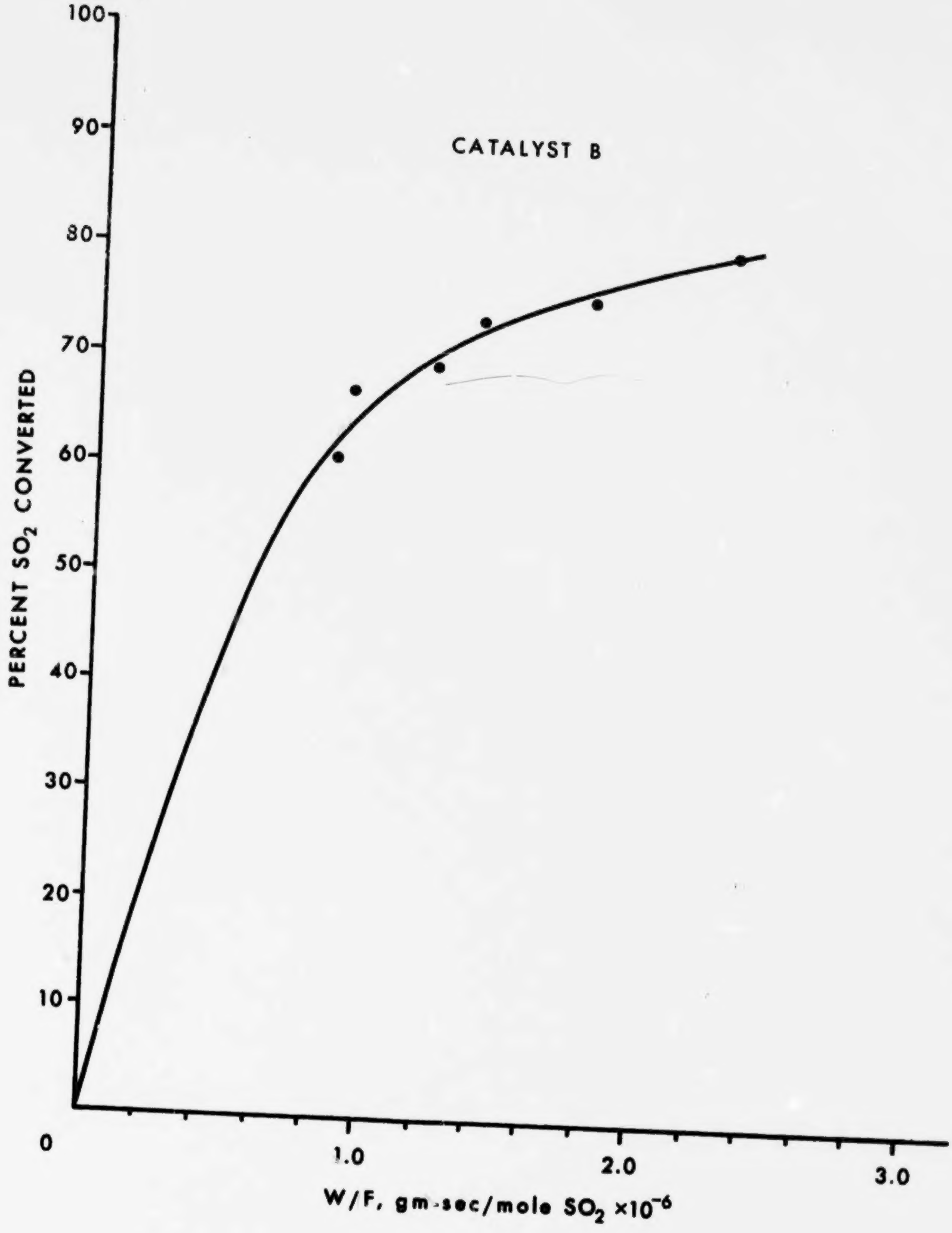


Figure 50. Effect of W/F on Conversion with Catalyst-B at 800°F

Table 35

CATALYST-B TEST RESULTS

Run No.	% SO_2 in feed (mole)	Catalyst Weight (gms)	Total Flow (cc/sec)	W/F $(\frac{\text{gm-sec}}{\text{cc}})$	W/F $(\frac{\text{gm-sec}}{\text{mole } SO_2})$	Temp. (°F)	% Conversion
1	.300	8.5	30	.283	2.30	800	80.2
2	.292	8.5	40	.213	1.78	800	75.3
3	.302	8.5	50	.170	1.38	800	73.4
4	.286	8.5	60	.142	1.21	800	69.1
5	.325	8.5	70	.121	.91	800	66.5
6	.302	8.5	80	.106	.86	800	60.6
7	.293	8.5	30	.283	2.36	850	89.0
8	.285	8.5	40	.213	1.82	850	83.5
9	.301	8.5	50	.170	1.37	850	80.9
10	.302	8.5	60	.142	1.15	850	73.9
11	.322	8.5	70	.121	.92	850	71.5
12	.305	8.5	80	.106	.85	850	69.0
13	.309	8.5	30	.283	2.24	900	89.0
14	.295	8.5	40	.213	1.76	900	87.0
15	.302	8.5	50	.170	1.37	900	85.2
16	.307	8.5	60	.142	1.13	900	82.7
17	.304	8.5	70	.121	.97	900	80.0
18	.314	8.5	80	.106	.82	900	77.1

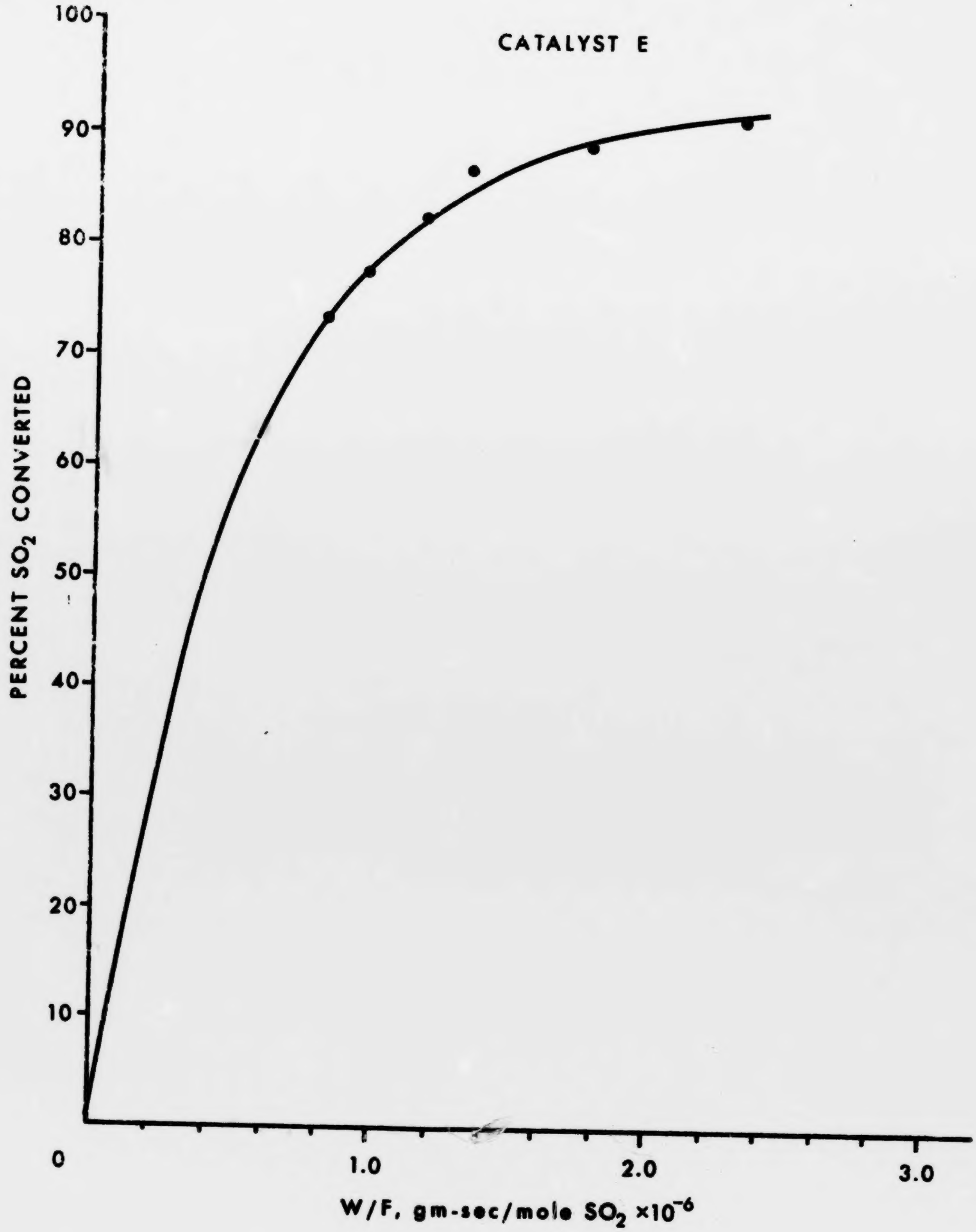


Figure 51. Effect of W/F on Conversion with Catalyst-E at 900°F

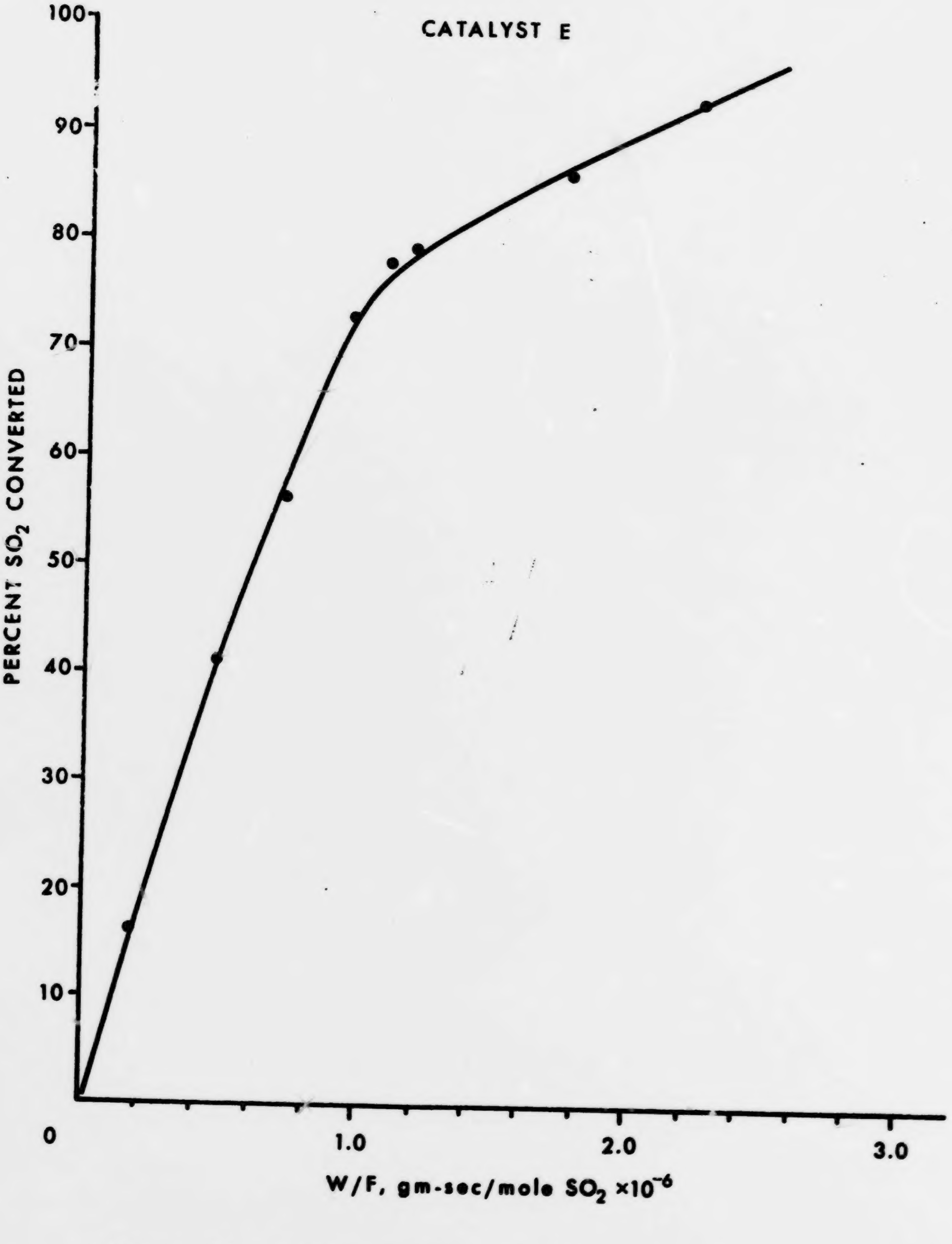


Figure 52. Effect of W/F on Conversion with Catalyst-E at 850°F

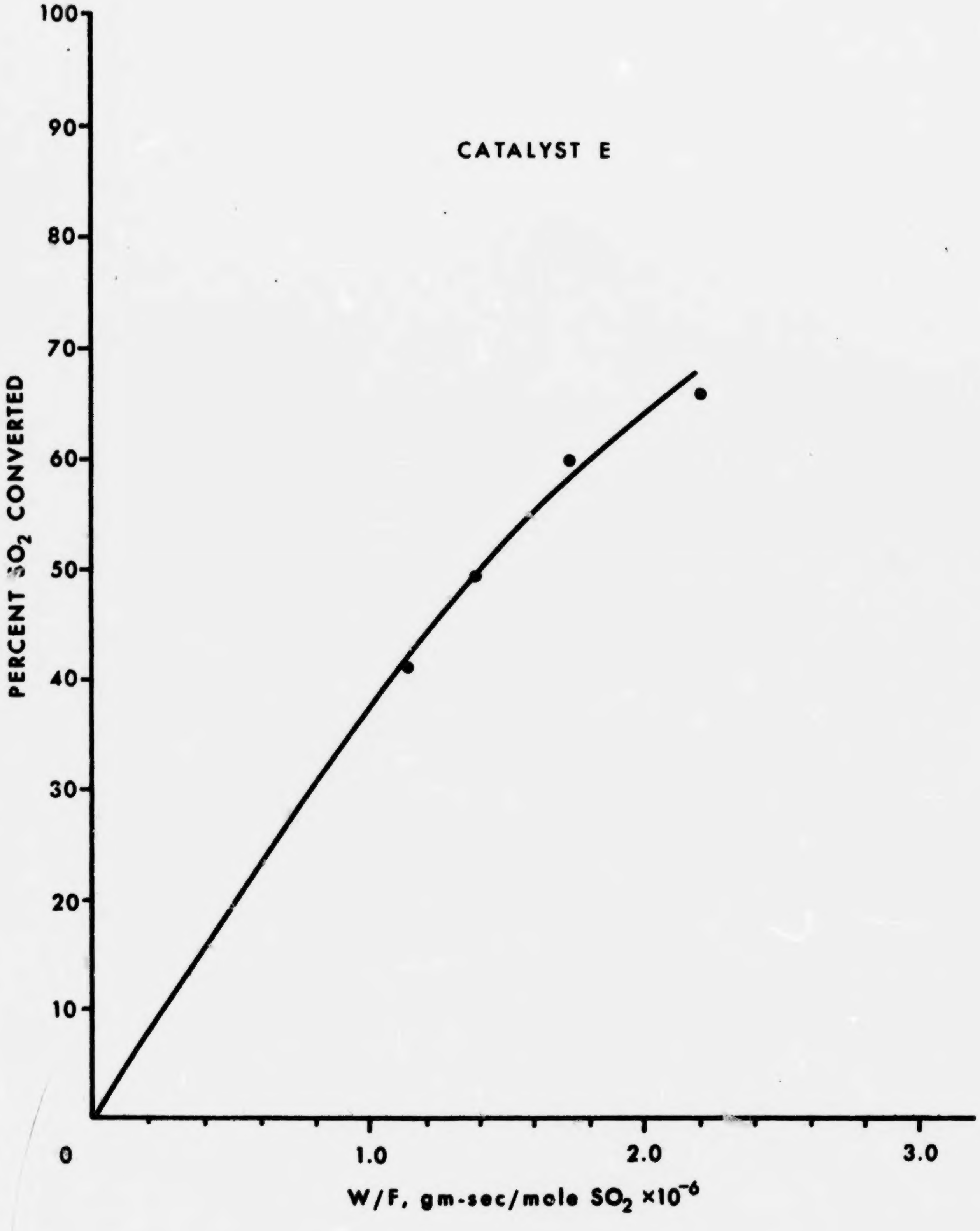


Figure 53. Effect of W/F on Conversion with Catalyst-E at 800°F

Table 36

CATALYST-E TEST RESULTS

Run No.	% SO_2 in feed (mole)	Catalyst Weight (gms)	Total Flow (cc/sec)	W/F $(\frac{gm\text{-}sec}{cc})$	W/F $(\frac{gm\text{-}sec}{mole\ SO_2})$	Temp. (°F)	% Conversion
1	.314	8.5	30	.283	2.20	800	65.3
2	.299	8.5	50	.170	1.39	800	49.2
3	.301	8.5	40	.213	1.73	800	59.5
4	.303	8.5	60	.142	1.14	800	40.9
5	.309	8.5	30	.283	2.23	850	92.7
6	.297	8.5	40	.213	1.75	850	85.7
7	.314	5.0	40	.125	.97	850	72.6
8	.348	8.5	50	.170	1.19	850	78.6
9	2.0	8.5	60	.142	.17	850	16.0
10	.315	8.5	60	.142	1.10	850	77.4
11	.280	5.0	60	.083	.726	850	56.0
12	.315	5.0	80	.063	.48	850	41.0
13	.299	8.5	30	.283	2.31	900	91.0
14	.296	8.5	40	.213	1.76	900	88.7
15	.312	8.5	50	.170	1.33	900	86.3
16	.296	8.5	60	.142	1.17	900	81.9
17	.309	8.5	70	.121	.96	900	77.0
18	.314	8.5	80	.106	.82	900	72.9

APPENDIX II

EXPERIMENTAL CATALYST TEST DATA

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Table 37

Catalyst Code	Catalyst	Type of Support	Promoter	wt% Support Material	wt% Catalyst	wt% Promoter	Gas Flow Rate cc/sec	SO_2 Conc. %	W/F	Conversion Efficiency %
75°F										
MES-1	SnO_2	Fuller's Earth	None	92	8	---	40	0.317	1.49	19.2*
MEB-1	BaO	" "	"	92	8	---	40	0.312	1.46	19.2*
MEC-1	Cr_2O_3	" "	"	92	8	---	40	0.292	1.57	17.1*
MECB-1	BaO	" "	"	92	4	---	40	0.295	1.48	14.6*
	SnO_2	" "	"	92	4	---	40			
MEBC-1	Cr_2O_3	" "	"	92	4	---	40	0.293	1.40	14.0*
	BaO	" "	"	92	4	---	40			
454DX1-10	V_2O_5	" "	SeO_2	72	8	20	40	0.281	0.23	2.1
150°F										
MECV-2	V_2O_5	Fuller's Earth	$CuSO_4$	72	8	20	40	0.300	1.61	22.3
MEAV-1	V_2O_5	" "	$(NH_4)_2SO_4$	72	8	20	40	0.301	1.60	14.0
MEAV-1	V_2O_5	" "	$(NH_4)_2SO_4$	72	8	20	40	0.301	1.60	8.6
MECV-2	V_2O_5	" "	$CuSO_4$	72	8	20	40	0.300	1.61	2.0
454DX1-10	V_2O_5	" "	SeO_2	72				0.303	0.22	0.3
200°F										
MEFV-2	$V_2O_5 \cdot Fe_2O_3$	Fuller's Earth	NaSCN	72	8	20	40	0.312	1.56	1.3
MENV-1	V_2O_5	" "	NaSCN	72	8	20	40	0.306	1.68	0.6
225°F										
MENV-2	V_2O_5		KSCN	72	8	20	40	0.320	1.64	1.3
250°F										
MEFV-2	$V_2O_5 \cdot Fe_2O_3$		NaSCN	72	8	20	40	0.311	1.57	1.6
MENV-1	V_2O_5		NaSCN	72	8	20	40	0.304	1.69	0.9
300°F										
MEFV-2	$V_2O_5 \cdot Fe_2O_3$	Fuller's Earth	NaSCN	72	8	20	40	0.310	1.57	2.6
MEKV-6	V_2O_5	" "	K_2SO_4	72	8	20	40	0.312	1.55	2.5
MENV-2	V_2O_5	" "	KSCN	72	8	20	40	0.324	1.62	2.2
MENV-1	V_2O_5	" "	NaSCN	72	8	20	40	0.307	1.67	1.3
454DX1-10	V_2O_5	" "	SeO_2	72	8	20	40	0.311	0.22	0.6
MES-2	SeO_2	" "	-----	92	8		40	0.319	1.35	0.0
350°F										
MEPV-4	V_2O_5	Al_2O_3 (Acid)	K_2CO_3	72	8	20	40	0.298	1.49	45.6
MEPV-4	V_2O_5	Al_2O_3 (Acid)	K_2CO_3	72	8	20	40	0.298	1.49	18.1
MENV-1	V_2O_5	Fuller's Earth	NaSCN	72	8	20	40	0.308	1.66	7.3
MEFV-2	$V_2O_5 \cdot Fe_2O_3$	" "	NaSCN	72	8	20	40	0.307	1.59	5.5
MECV-2	$V_2O_5 \cdot Fe_2O_3$	" "	$CuSO_4$	72	8	20	40	0.298	1.62	1.9
MESV-1.	$V_2O_5 \cdot Fe_2O_3$	" "	SeO_2	72	8	20	40	0.298	1.48	0.0
400°F										
MEFV-2	$V_2O_5 \cdot Fe_2O_3$	Fuller's Earth	NaSCN	72	8	20	40	0.303	1.61	7.3
MELV-1	V_2O_5	Fuller's Earth	$LiHSO_4$	72	8	20	40	0.315	1.77	1.9
MENV-1	V_2O_5	Fuller's Earth	NaSCN	72	8	20	40	0.302	1.70	1.7
454DX1-10	V_2O_5	Fuller's Earth	SeO_2	72	8	20	40	0.297	0.23	1.4
450°F										
MEKM-1	MnO_2	Fuller's Earth	KHSO	72	8	20	40	0.301	1.66	1.[illegible]
MEKV-1	V_2O_5	Fuller's Earth	KHSO	72	8	20	40	0.309	1.88	1.0
475°F										
MELV-1	V_2O_5	Fuller's Earth	LiHSO	72	8	20	40	0.316	1.77	1.3
500°F										
MEKV-1	V_2O_5	Fuller's Earth	$KHSO_4$	72	8	20	40	0.313	1.85	1.3
MEKM-2	MnO_2	Alumina	$KHSO_4$	72	8	20	40	0.282	1.95	1.1
MESV-1	V_2O_5	Fuller's Earth	SeO_2	72	8	20	40	0.298	1.48	.0
MEPV-4	V_2O_5	Al_2O_3 (acid)	K_2CO_3	72	8	20	40	0.298	1.49	0.0
550°F										
MEFF-1	Fe_2O_3	Fuller's Earth	$Fe_2(SO_4)_3$	72	8	20	40	0.319	1.57	1.6
MEFV-1	V_2O_5	" "	$KHSO_4$	72	4	20	40	0.278	1.91	1.4
	Fe_2O_3	" "			4					
MEBV-1	V_2O_5	" "	Bi_2O_3	88	8	4	40	0.284	1.63	1.4
MEKV-1	V_2O_5	" "	$KHSO_4$	72	8	20	40	0.310	1.93	1.3

Table 37 (Cont'd)

Catalyst Code	Catalyst	Type of Support	Promoter	wt% Support Material	wt% Catalyst	wt% Promoter	Gas Flow Rate cc/sec	SO_2 Conc. %	W/F	Conversion Efficiency %
				575°F						
[illegible]	SeO_2	Fuller's Earth	---	92	8	---	40	0.323	1.34	3.4
				600°F						
514CP-2X3	Cr-Ba-Sn	----	----	----	----	----	40	0.301	1.62	92.0●
MEPV-5	V_2O_5	Fuller's Earth	K_2CO_3 $KHSO_4$	72	8	10 10	40	0.316	1.87	75.1
MERV-5	V_2O_5	" "	$KHSO_4$	72	8	10	40	0.316	1.87	46.2
MEFF-1	Fe_2O_3	" "	Potash	72	8	20	40	0.303	1.52	38.6●
MEFV-3	V_2O_5	" "	K_2CO_3 $KHSO_4$	72	8	10 10	40	0.309	1.31	34.3
[illegible]-68-411	Pt	Alumina	----	----	----	----	40	0.301	1.64	24.[illegible]●
MEKV-2	V_2O_5	Fuller's Earth	$KHSO_4$	72	8	20	40	0.298	1.74	30.2
MEF[illegible]-3	V_2O_5	" "	$KHSO_4$	72	8	20	40	0.309	1.31	20.1●
MEBC-2	CuO BaO	" "	None	84	8	None	40	0.307	1.59	20.0●
MEKV-1q	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.315	1.84	15.[illegible]●
MEBC-3	CuO BaO	" "	$KHSO_4$	64	8	20	40	0.307	1.71	15.0●
MEKV-12	V_2O_5	" "	Cs-Rb-K	72	8	20	40	.323	1.41	10.8
MEFV-1-K 600	V_2O_5	" "	Rb_2SO_4 K_2SO_4	76	8	8 8	40	.288	1.58	9.0
514CP-4	Pt-Fe	Alumina	----	----	----	----	40	0.303	1.53	8.9
MEKV-1F	V_2O_5	Fuller's Earth	Rb_2SO_4	72	8	20	40	0.312	1.86	8.8
MERV-1c	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.313	1.85	8.5
514CP-3	Pt-Fe	Alumina	----	----	----	----	40	0.301	1.22	8.0
HF-1	Pt	Alumina	$Fe_2(SO_4)_3$	----	----	----	40	0.299	1.29	8.0
MEKV-12-600	V_2O_5	Fuller's Earth	Rb-Cs-K	72	8	20	40	0.313	1.45	7.2
MECV-1	CuO V_2O_5	" "	$KHSO_4$	64	8	20	40	0.317	1.50	6.9
514CP-2	Pt-Fe	Alumina	----	----	----	----	40	0.303	1.05	6.9
MEKV-10-600	V_2O_5	Fuller's Earth	Cs-Rb	72	8	20	40	.334	1.36	6.5
MEPV-1	V_2O_5	" "	Potash	72	8	20	40	0.295	1.59	6.4
MEKV-4	V_2O_5	" "	$KHSO_4$	76	4	20	40	0.301	1.56	6.3
MECV-3K 600	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.334	1.53	5.7
MECV-3C	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.334	1.74	5.1
MEKV-8-600	V_2O_5	" "	Cs-Rb-K	72	8	20	40	0.335	1.36	5.1
MEPZ-1	ZnO	" "	Potash	72	8	20	40	0.301	1.62	5.1
MEPM-1	MoO_3	" "	Potash	72	8	20	40	0.303	1.53	5.0
MERV-3	V_2O_5	" "	$KHSO_4$	72	8	20	40	0.299	1.69	5.0
MECV-3	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.318	1.46	4.6
MEKV-9-600	V_2O_5	" "	Cs-Rb-K	72	8	20	40	0.334	1.36	4.5
MERV-1	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.312	-.32	4.5
MEKV-7-600	V_2O_5	" "	Cs-Rb-K	72	8	20	40	0.319	1.42	4.4
MEKV-11-600	V_2O_5	" "	Cs-Rb-K	72	8	20	40	0.301	1.51	4.3
MEFV-4	V_2O_5 Fe_2O_3	" "	$Fe_2(SO_4)_3$	72	4 4	20	40	0.300	1.67	4.0
MECV-3b'	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.331	1.75	3.9
MESC-1	CuO SnO_2	" "	None	84	8	None	40	0.323	1.47	3.7
MEF-1	Fe_2O_3	" "	----	80	20	----	40	0.307	1.49	3.6
MEFV-3	V_2O_5	" "	$Fe_2(SO_4)_3$	72	8	20	40	0.305	1.41	3.6
MEKV-6	V_2O_5	" "	K_2SO_4	72	8	20	40	0.312	1.55	3.6
MEMV-1	V_2O_5 MoO_3	" "	----	84	8 8	----	40	0.300	1.60	3.3
MEM-1	MoO_3	" "	----	80	20	----	40	0.308	1.51	3.2
MECP-2	Fe_2O_3 Cr_2O_3	" "	$KHSO_4$	64	8	20	40	0.293	1.72	3.1
MECF-3	Fe_2O_3 CuO	" "	----	84	8	----	40	0.295	1.54	3.1
MECV-3a	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.324	1.79	3.1
MENY-3	V_2O_5	" "	Na_2SO_4	72	8	20	40	0.321	1.38	3.1
MEWV-1	V_2O_5 WO_3	" "	----	84	8 8	----	40	0.297	1.58	3.0
MEZF-1	Fe_2O_3 ZnO	" "	----	84	8 8	----	40	0.302	1.60	3.0
MEZV-1	V_2O_5 ZnO	" "	----	84	8 8	----	40	0.317	1.59	2.8
MEMF-1	Fe_2O_3 MoO_3	" "	----	84	8	----	40	0.302	1.63	2.6
MELV-2	V_2O_5	" "	Li_2SO_4	72	8	20	40	0.324	1.29	2.5
MECF-4	Fe_2O_3 CuO	" "	$KHSO_4$	64	8	20	40	0.290	1.71	2.3
MECC-1	CuO Cr_2O_3	" "	----	84	8 8	----	40	0.294	1.69	2.0
MESC-2	CuO SnO_2	" "	$KHSO_4$	64	8	20	40	0.319	1.73	1.9
MELV-1	V_2O_5	" "	$LiHSO_4$	72	8	20	40	0.295	1.89	1.7
MEST-1	Ta_2O_5	" "	Na_2SeO_4	72	8	20	40	0.319	1.46	1.6
MECC-2	CuO Cr_2O_3	" "	$KHSO_4$	64	8	20	40	0.293	1.80	1.4
MEFV-5	V_2O_5 Fe_2O_3	" "	----	84	8 8	----	40	0.293	1.64	1.4
MEKM-1	MnO_2	" "	$KHSO_4$	72	8	----	40	0.296	1.69	1.4
MEBV-1	V_2O_5	" "	Bi_2O_3	88	8	4	40	0.292	1.59	1.0
MEKV-1	V_2O_5	" "	$KHSO_4$	72	8	20	40	0.295	1.96	1.0
MEBV-2	V_2O_5 B_2O_3	" "	----	84	8	----	40	0.319	1.34	0.0
MECF-1	Fe_2O_3 Cr_2O_3	" "	$KHSO_4$	64	8	20	40	0.292	1.78	0.0
MEKV-5	V_2O_5	SK-410	$KHSO_4$	72	8	20	40	0.309	1.72	0.0
MEPV-2	V_2O_5	Fuller's Earth	K_2CO_3	72	8	20	40	----	----	----

Table 37 (Cont'd)

Catalyst Code	Catalyst	Type of Support	Promoter	wt% Support Material	wt% Catalyst	wt% Promoter	Gas Flow Rate cc/sec	SO_2 conc. %	W/F	Conversion Efficiency %
				650°F						
514CP-1	Pt·Pd	Alumina	---	---	---	---	40	0.300	2.30	40.7
515CP-1	Pt	Alumina	---	---	---	---	40	0.289	1.77	37.0
MEFV-1	V_2O_5	Fuller's Earth	Potash	72	8	20	40	0.315	1.49	3.8
				700°F						
MP-1	Pt	Alumina	$Fe_2(SO_4)_3$	----	----	----	40	0.310	1.11	32.5
MERV-1-K-600	V_2O_5	Fuller's Earth	Rb-K	72	8	20	40	0.341	1.33	6.5
MENP-1	Pt	Alumina	NaSCN	----	----	----	40	0.303	1.94	15.5
514-CP-4	Pt	----	----	----	----	----	40	0.288	1.61	12.8
MEKV-12	V_2O_5	Fuller's Earth	C_s-Rb-K	72	8	20	40	0.323	1.41	11.2
MEKV-7-600	V_2O_5	" "	C_s-Rb-K	72	8	20	40	0.346	1.31	10.7
MECV-3-K-600	V_2O_5	" "	C_s-K	72	8	20	40	0.343	1.32	10.6
MEKV-12-600	V_2O_5	" "	C_s-Rb-K	72	8	20	40	0.349	1.45	10.3
514-CP-3	Pt	----	----	----	----	----	40	0.287	1.28	8.7
MEKV-8-600	V_2O_5	Fuller's Earth	C_s-Rb-K	72	8	20	40	0.347	1.31	8.5
514-CP-2	Pt	----	----	----	----	----	40	0.294	1.08	8.2
MEKV-11-600	V_2O_5	Fuller's Earth	C_s-Rb-K	72	8	20	40	0.341	1.33	6.9
MEKV-9-600	V_2O_5	" "	C_s-Rb-K	72	8	20	40	0.327	1.39	6.6
MEKV-10-600	V_2O_5	" "	C_s-Rb-K	72	8	20	40	0.334	1.36	6.5
MEFP-1	Fe_2O_3	" "	$Fe_2(SO_4)_3$	72	8	20	40	0.312	1.60	6.1
MEFV-4	V_2O_5 Fe_2O_3	" "	$Fe_2(SO_4)_3$	72	4 4	20	40	0.321	1.56	5.6
MEFV-3	Fe_2O_3 Fe_2O_3	" "	$Fe_2(SO_4)_3$	72	8	20	40	0.310	1.39	5.5
MEST-1	Ta_2O_5	" "	Na_2SeO_4	72	8	20	40	0.288	1.61	5.2
MEKV-4	V_2O_5	" "	$KHSO_4$	76	4	20	40	0.306	1.42	4.3
MEFV-1	V_2O_5	" "	Potash	72	4	20	40	0.300	1.56	3.5
MEKV-2	V_2O_5	" "		74	6	20	40	0.320	1.62	3.1
MEKV-1	V_2O_5	" "		72	8	20	40	0.312	1.85	2.9
MELV-1	V_2O_5	" "	$LiHSO_4$	72	8	20	40	0.307	1.82	2.6
MEFV-1	V_2O_5 Fe_2O_3	" "		72	4 4	20	40	0.311	1.70	2.3
MEKV-1										2.3
MEMV-1	V_2O_5 MoO_3	" "	None	84	8 6	----	40	0.310	1.55	2.3
MEKV-3	V_2O_5	" "		72	8	20	40	0.302	1.55	2.3
MEF-1	Fe_2O_3	" "	None	80	20	----	40	0.307	1.49	2.0
MEZV-1	V_2O_5 ZnO	" "	None	84	8 8	----	40	0.305	1.66	2.0
MEM-1	MoO_3	" "	None	80	20	----	40	0.304	1.53	2.0
MEKM-2	MnO_2	Alumina		72	8	20	40	0.299	1.69	2.0
MEZF-1	Fe_2O_3 ZnO	Fuller's Earth	None	84	6	----	40	0.312	1.56	1.9
MEMF-1	Fe_2O_3 MoO_3	" "	None	84	8 8	----	40	0.309	1.60	1.9
MEFV-5	V_2O_5	" "	None	84	8	----	40	0.311	1.55	1.6
MEWV-1	V_2O_5 WO_3	" "	None	84	8	----	40	0.303	1.55	1.3
MEBV-1	V_2O_5	" "	Bi_2O_3	88	8	4	40	0.302	1.54	1.3
MEKV-5	V_2O_5	" "		72	8	20	40	0.309	1.72	1.0
MEBV-2	V_2O_5 B_2O_3	" "	None	84	8	----	40	0.316	1.35	0.9
MEV-1	V_2O_5	" "	None	92	8	----	40	0.305	1.42	0.7
MEKM-1	MnO_2	" "	$KHSO_4$	72	8	20	40	0.301	1.66	0.3
				750°F						
MECV-3	V_2O_5	Fuller's Earth	Cs_2SO_4	72	8	2	40	0.297	1.57	19.9•
MEKV-4	V_2O_5	Al_2O_3 (acid)	K_2CO_3	72	8	2	40	0.298	1.49	15.1
				800°F						
514CP-1	Pt Pd	Alumina	----	----	----	----	40	0.290	1.79	60.[illegible]
MP-1	Pt	"	$Fe_2(SO_4)_3$	----	----	----	40	0.295	1.05	59.4
515CP-1	Pt	"	----	----	----	----	40	0.292	1.32	63.0
MENP-1	Pt	"	NaSCN	----	----	----	40	0.306	1.91	60.1
514CP-4	Pt	----	----	----	----	----	40	0.305	1.52	27.9
514CP-2	Pt	----	----	----	----	----	40	0.296	1.07	27.0
514CP-3	Pt	----	----	----	----	----	40	0.308	1.19	26.3
MEKV-5	V_2O_5	Fuller's Earth	$KHSO_4$	72	8	20	40	0.309	1.72	10.7
MEFP-1	Fe_2O_3	" "	$Fe_2(SO_4)_3$	72	8	20	40	0.324	1.54	6.6
MEFV-4	V_2O_5 Fe_2O_3	" "	$Fe_2(SO_4)_3$	72	4 4	20	40	0.291	1.72	7.9•
MEPV-1	V_2O_5	" "	Potash	72	8	20	40	0.313	1.50	7.4
MEFV-3	V_2O_5	" "	$Fe_2(SO_4)_3$	72	8	20	40	0.292	1.48	6.5
MEKV-2	V_2O_5	" "	$KHSO_4$	74	6	20	40	0.301	1.59	6.3
MEKV-3	V_2O_5	" "	$KHSO_4$	72	8	20	40	0.284	1.62	6.2
MEKV-1	V_2O_5	" "	$KHSO_4$	72	8	20	40	0.289	1.60	5.9
MEKV-4	V_2O_5	" "	$KHSO_4$	76	4	20	40	0.269	1.50	5.4
MEFV-1	V_2O_5 Fe_2O_3	" "	$KHSO_4$	72	4 4	20	40	0.295	1.61	4.1
MELV-1	V_2O_5	" "	$LiHSO_4$	72	8	20	40	0.301	1.85	4.0
MEFV-5	V_2O_5 Fe_2O_3	" "	None	84	8 8	----	40	0.318	1.51	3.5
MEZF-1	Fe_2O_3 ZnO	" "	None	84	8 8	----	40	0.292	1.66	3.1
MEF-1	Fe_2O_3	" "	None	80	20	----	40	0.306	1.50	2.6
MEMF-1	Fe_2O_3 MoO_3	" "	None	84	8 8	----	40	0.317	1.56	2.5
MEBV-1	V_2O_5	" "	Bi_2O_3	88	8	4	40	0.315	1.46	1.9
MEKM-2	MnO_2	Alumina	$KHSO_4$	72	8	20	40	0.316	1.60	1.9
MEZV-1	V_2O_5 ZnO	Fuller's Earth	None	84	8 8	20	40	0.302	1.67	1.7

Table 37 (Cont'd)

Catalyst Code	Catalyst	Type of Support	Promoter	wt% Support Material	wt% Catalyst	wt% Promoter	Gas Flow Rate cc/sec	SO_2 Conc. %	W/F	Conversion Efficiency %
MKWV-1	V_2O_5 WO_3	" "	None	84	8 8	20	40	0.301	1.56	1.7
MKV-1	V_2O_5	" "	None	92	8	----	40	0.320	1.36	1.6
MEKM-1	MnO_2	" "	$KHSO_4$	72	8	20	40	0.304	1.65	1.6
MLM-1	MoO_3	" "	None	80	20	----	40	0.324	1.44	1.5
MLBV-2	V_2O_5 B_2O_3	" "	None	84	8	----	40	0.295	1.45	1.4
MLMV-1	V_2O_5 MoO_3	" "	None	84	8 8	----	40	0.300	1.60	1.3

850°F

Catalyst Code	Catalyst	Type of Support	Promoter	wt% Support Material	wt% Catalyst	wt% Promoter	Gas Flow Rate cc/sec	SO_2 Conc. %	W/F	Conversion Efficiency %
MKV-1	V_2O_5	Fuller's Earth	---	92	8	---	40	0.315	1.38	10.5

900°F

Catalyst Code	Catalyst	Type of Support	Promoter	wt% Support Material	wt% Catalyst	wt% Promoter	Gas Flow Rate cc/sec	SO_2 Conc. %	W/F	Conversion Efficiency %
MLPV-6	V_2O_5	Al_2O_3(acid)	$KHSO_4$	72	8	10	40	0.320	1.84	82.7
MP-1	Pt	Alumina	$Fe_2(SO_4)_3$	----	----	----	40	0.295	1.11	76.9
MKFV-4-500	V_2O_5	Al_2O_3(acid)	K_2CO_3	72	8	20	40	0.293	1.53	73.6
MLNP-1	Pt	Alumina	NaSCN	----	----	----	40	0.294	1.99	68.0
S14CP-3	Pt	----	----	----	----	----	40	0.302	1.21	67.7
S14CP-2	Pt	----	----	----	----	----	40	0.303	1.09	67.7
MLFV-5	V_2O_5	Al_2O_3(acid)	$KHSO_4$	72	8	10	40	0.320	1.84	65.4
MKFV-6	V_2O_5	"	K_2CO_3	72	8	20	40	0.279	1.60	63.4*
MLRV-1-600	V_2O_5	Fuller's Earth	Rb_2SO_4	72	8	20	40	0.298	1.95	58.7
MKRV-1e	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.294	1.98	54.8*
MKCV-3a	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.287	2.02	53.3
MKRV-1f	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.296	1.96	53.5*
S14CP-4	Pt	----	----	----	----	----	40	0.302	1.54	49.7
MLRV-1g	V_2O_5	Fuller's Earth	Rb_2SO_4	72	8	20	40	0.298	1.95	46.1*
MKCV-3b	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.286	2.03	44.1*
MLCV-3	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.295	1.58	43.7
MLRV-1-400	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.294	1.98	43.7
MLFV-7	V_2O_5	" "	$KHSO_4$	72	8	10	40	0.296	1.37	43.2
MKCV-3-400	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.287	2.02	43.0
MLFV-4	V_2O_5	Al_2O_3(acid)	K_2CO_3	72	8	20	40	0.279	1.60	41.6
MKCV-3-500	V_2O_5	Fuller's Earth	Cs_2SO_4	72	8	20	40	0.286	2.03	38.9
MKRV-1-500	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.296	1.96	37.1
MLPZ-1	ZnO	" "	Potash	72	8	20	40	0.302	1.62	36.1*
MLRV-1	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.320	1.29	35.6
MKCV-3c	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.297	1.96	33.3*
MKPM-1	MoO_3	" "	Potash	72	8	20	40	0.299	1.55	31.8*
MKFV-3	V_2O_5	" "	$KHSO_4$	72	8	10	40	0.296	1.37	31.4
MKCV-3-600	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.297	1.96	30.5
MLCV-3	V_2O_5	" "	Cs_2SO_4	72	8	20	40	0.318	1.46	30.2
MKRV-1	V_2O_5	" "	Rb_2SO_4	72	8	20	40	0.320	1.29	30.0
MLKV-5	V_2O_5	SK-410	$KHSO_4$	72	8	20	40	0.309	1.72	29.9
MKFV-4a	V_2O_5	Al_2O_3(acid)	K_2CO_3	72	8	20	40	0.293	1.55	25.4
MLRV-1-500	V_2O_5	Fuller's Earth	Rb_2SO_4	72	8	20	40	0.297	1.39	25.2
MLPZ-1	ZnO	" "	Potash	72	8	20	40	0.302	1.62	15.6
MLKV-3	V_2O_5	" "	$KHSO_4$	72	8	20	40	0.287	1.63	13.9
MLKV-2	V_2O_5	" "	$KHSO_4$	74	6	20	40	0.304	1.57	12.8
MLKV-4	V_2O_5	" "	$KHSO_4$	76	4	20	40	0.286	1.52	12.2
MKPV-1	V_2O_5	" "	Potash	72	8	20	40	0.296	1.58	11.8
MLFF-1	Fe_2O_3	" "	$Fe_2(SO_4)_3$	72	8	20	40	0.299	1.67	11.4
VLFV-4	V_2O_5 Fe_2O_3	" "	$Fe_2(SO_4)_3$	72	4 4	20	40	0.301	1.66	10.9*
MLKV-1	V_2O_5	" "	$KHSO_4$	72	8	20	40	0.304	1.90	9.3
MLSV-5	V_2O_5	" "	Na_2SO_4	72	8	20	40	0.322	1.38	9.1
MLFV-3	V_2O_5	" "	$Fe_2(SO_4)_3$	72	8	20	40	0.299	1.44	9.0
MLLV-1	V_2O_5	" "	$LiHSO_4$	72	8	20	40	0.306	1.53	7.2
MLFV-1	V_2O_5 Fe_2O_3	" "	$KHSO_4$	72	4 4	20	40	0.297	1.78	6.4
MLLV-2	V_2O_5	" "	Li_2SO_4	72	8	20	40	0.318	1.31	6.3
MLF-1	Fe_2O_3	" "	None	80	20	----	40	0.295	1.56	5.8
MLFV-6	V_2O_5 Fe_2O_3	" "	None	84	8 8	----	40	0.301	1.55	5.6
MLZF-1	Fe_2O_3 ZnO	" "	None	84	8 8	----	40	0.302	1.60	4.8
MLMF-1	Fe_2O_3 MoO_3	" "	None	84	8 8	----	40	0.300	1.64	4.7
MLKM-1	MnO_2	" "	$KHSO_4$	72	8	20	40	0.293	1.71	3.5
MLWV-1	V_2O_5 WO_3	" "	None	84	8 8	----	40	0.304	1.54	3.0
MLMV-1	V_2O_5 MoO_3	" "	None	84	8 8	----	40	0.303	1.59	3.0
MLV-1	V_2O_5	" "	None	92	8	----	40	0.302	1.44	3.0
MLBV-1	V_2O_5	" "	Bi_2O_3	88	8	4	40	0.298	1.56	3.0
MLZV-1	V_2O_5 ZnO	" "	None	84	8 8	----	40	0.301	1.68	2.7
MLKM-2	MnO_2	Alumina	$KHSO_4$	72	8	20	40	0.293	1.72	2.2
MLM-1	MoO_3	Fuller's Earth	None	80	20	----	40	0.297	1.57	1.7
MLBV-2	V_2O_5 B_2O_3	" "	None	84	8 8	----	40	0.299	1.41	1.3

APPENDIX III

EFFECT OF CATALYST PARTICLE GEOMETRY ON PRESSURE DROP IN A FIXED BED

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EFFECT OF CATALYST PARTICLE GEOMETRY ON PRESSURE DROP IN A FIXED BED

In selecting the geometrical form for catalyst particles in a fixed-bed reactor, several factors require balancing. It is desired to minimize pressure drop through the bed within the limits allowed by contact time requirement and gas velocity, minimize catalyst attrition rate, and minimize catalyst cost (i.e., not increase cost due to unusual geometry).

A computer program was written to calculate pressure drop as an aid in the design of the catalytic reactor. Three equations were included in the program based on the magnitude of the Reynolds number. For laminar flow through the catalyst bed ($Re < 10.0$) the equation becomes (Ref. 1).

$$\Delta P = \frac{200.0\ G \mu L\ \lambda^2\ (1.0-\delta)^2}{g\ D_p^2\ \rho\ \delta^3} \qquad (1)$$

The transient flow (Re 10.0- 200.0) equation is (Ref. 96):

$$\Delta P = \frac{2.0\ f\ G^n\ L\ \lambda^{(3-n)}\ (1.0-\delta)^{(3-n)}}{D_p^{(3-n)}\ g\ \rho\ \delta^3} \qquad (2)$$

where f and n are evaluated from a least squares fit of two graphs (Ref. 2) of Re versus f and Re versus n.

The turbulent flow ($Re > 200.0$) equation is (Ref. 3).

$$\Delta P = \frac{0.0243\ G^{1.9}\ \mu^{0.1}\ \lambda^{1.1}\ (1.0-\delta)}{g\ D_p^{1.1}\ \rho\ \delta^3} \qquad (3)$$

Each of the above is then converted to psi/ft by:

$$\Delta p = P/144.0$$

NOTATION

A = surface area of a pellet (sq ft)

D_p = effective particle diameter (ft)

G = mass velocity of gas (lb/sq ft hr)

L = length of bed (ft)

Re = modified Reynolds number ($D_p\ u\rho/\mu$)

V = volume of a pellet (cu ft)

f = modified friction factor

g = acceleration due to gravity (4.18×10^8 ft/hr^2)

n = state of flow factor

u = linear velocity of fluid (ft/sec)

δ = fractional voids in bed

ΔP = pressure drop (lb/sq in/ft)

λ = shape factor

μ = fluid viscosity (lb/hr/ft)

ρ = fluid density (lb/cu ft)

For the catalytic reactor of this report, all Reynolds numbers were in the turbulent flow range and equation (3) was used.

Three shapes were considered, those being, cylindrical, spherical, and granular. For the cylindrical case, the area and volume were found for three lengths and diameters were L/D = 1.0 (D = 1/8, 2/8, 3/8 in.) and the following calculations were made:

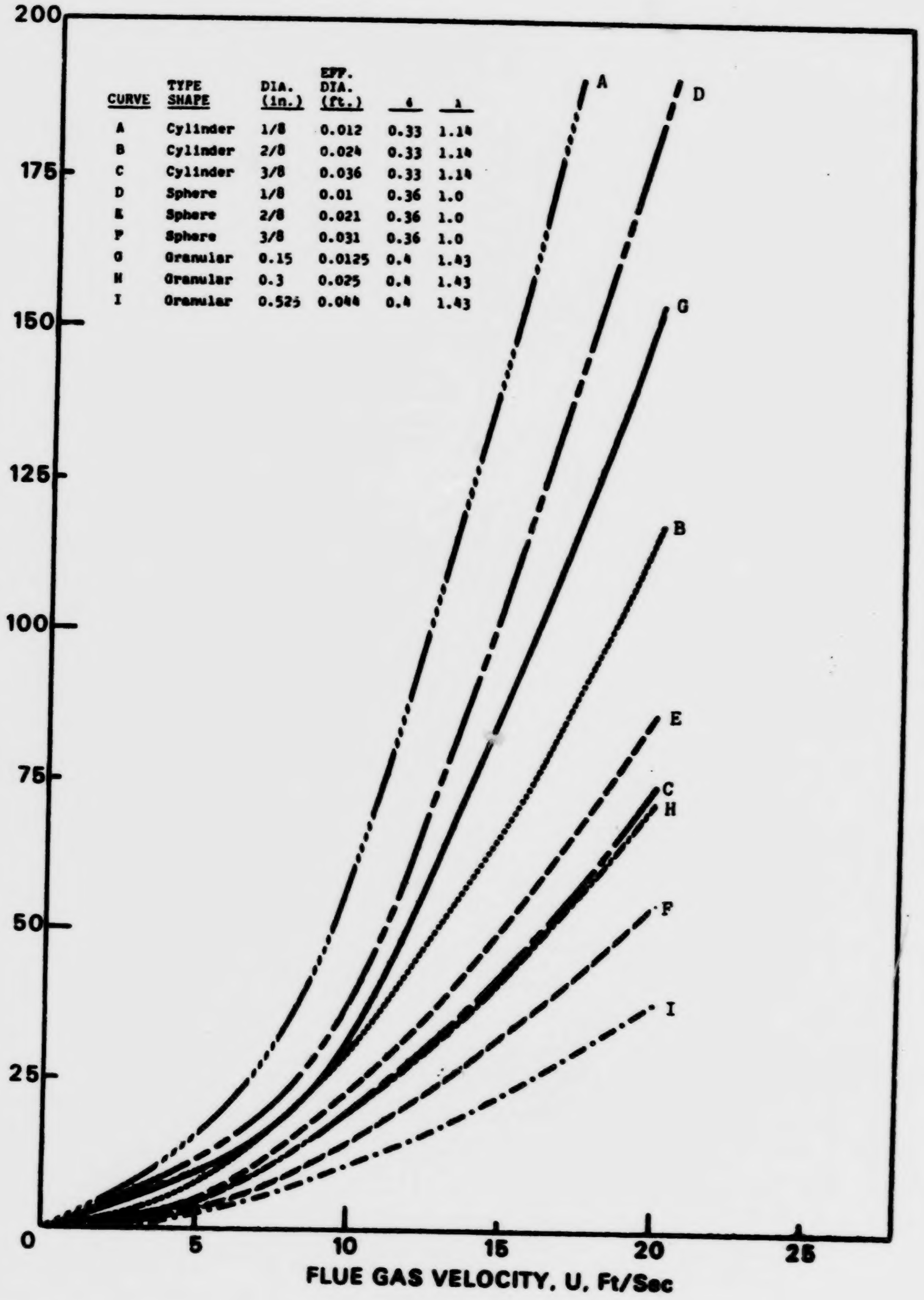
$$\lambda = \frac{0.205\ A}{V\ 2/3} \qquad \text{(Ref. 1)}$$

$$D_p = (6V/\pi)^{1/3}$$

$$\delta = 0.33$$

For the spherical case $\lambda = 1.0$; $D_p = 1/8, 2/8, 3/8$ in.; and $\delta = 0.36$. For the granular case $\lambda = 1.0/0.7$ (Ref. 98); $\delta = 0.4$; and $D_p = 0.15, 0.35, 0.525$ in.

Figure 54 summarizes the results of the study of the effect of catalyst particle geometry on pressure drop. Based on these comparative results, the suggested catalyst geometry is a cylinder about 3/8 inch in diameter with a length-to-diameter (L/D) ratio of 1 or 2. This is a common form for commercial catalysts. A spherical shape would result in lower pressure drop for equivalent diameter, but it is more costly to produce because of its shape. The granular shape, with still lower Δp response, is subject to higher attrition rate.



CURVE	TYPE SHAPE	DIA. (in.)	EFF. DIA. (ft.)	ϵ	λ
A	Cylinder	1/8	0.012	0.33	1.14
B	Cylinder	2/8	0.024	0.33	1.14
C	Cylinder	3/8	0.036	0.33	1.14
D	Sphere	1/8	0.01	0.36	1.0
E	Sphere	2/8	0.021	0.36	1.0
F	Sphere	3/8	0.031	0.36	1.0
G	Granular	0.15	0.0125	0.4	1.43
H	Granular	0.3	0.025	0.4	1.43
I	Granular	0.525	0.044	0.4	1.43

Figure 54. Effect of Catalyst Particle Geometry on Pressure Drop in a Fixed Bed

Table 38

```
*IOCS(CARD,1132 PRINTER)
*ONE WORD INTEGERS
*LIST SOURCE PROGRAM
C
C         PROGRAM TO CALCULATE PRESSURE DROP IN A CATALYTIC BED.
C         PROGRAM IS IN FORTRAN-IV FOR THE IBM 1130 8K WITH DISK.
C         THE EQUATION USED DEPENDS ON WHETHER THE GAS FLOW IS
C         LAMINER, TRANSIENT, OR TURBULENT.
C         THE REQUIRED PARAMETERS FOR THE EQUATIONS ARE-
C         EFFECTIVE DIAMETER OF THE PELLET(DIAP)
C         THE SHAPE FACTOR OF THE PELLET (ELMDA)
C         THE VOID SPACE OF THE REACTOR USING THESE PELLETS (DELTA)
C         THE GAS DENSITY (RHO)
C         THE GAS VISCOSITY (EMU)
C         THE VELOCITY OF THE GAS (U)
C         DP IS PRESSURE DROP IN LB./ SQ. IN./ FT.AND IS PER UNIT
C         MEASURE NOT PER REACTOR LENGTH
C
      DIMENSION TITLE(3,6)
      SG=4.18E08
      AL=1.0
C
C         ITERATE ON THE THREE DIFFERENT SHAPES
C
      DO 1 I=1,3
    1 READ(2,1010)(TITLE(I,J),J=1,6)
 1010 FORMAT(6A4)
C
      DO 70 J=1,3
      WRITE(3,10)(TITLE(J,K),K=1,6)
   10 FORMAT(10X,'PARAMETRIC STUDY OF PRESSURE DROP THROUGH CATALYTIC BE
     1D ',6A4/)
C
      GO TO (20,21,22),J
C
C         DEFINE THE REQUIRED PARAMETERS FOR THE CYLINDRICAL CASE
C
   20 CONTINUE
      DELTA=0.33
      HN=(1.0/8.0)/12.0
      R=HN/2.0
      V=3.142*R**2*HN
      A=6.284*R*HN+6.284*R**2
      DIAP=(6.0*V/3.142)**0.3333
      ELMDA=0.205*A/V**0.6667
      GO TO 23
C
C         DEFINE THE REQUIRED PARAMETERS FOR THE SPHERICAL CASE

   21 CONTINUE
      ELMDA=1.0
      DELTA=0.36
      DIAP=1.0/96.0
      GO TO 23
C
C         DEFINE THE REQUIRED PARAMETERS FOR THE GRANULAR CASE
C
   22 CONTINUE
      DELTA=0.4
      DIAP=0.15/12.0
      ELMDA=1.0/0.7
```

Table 38 (Cont'd)

```
C
   23 WRITE(3,1111)
 1111 FORMAT(10X,'EFF DIA (FT)','  LAMDA      ','  DELTA      ')
      WRITE(3,1110)DIAP,ELMDA,DELTA
 1110 FORMAT( 10X,E12.5,1X,F7.4,6X,F7.4)
C
C          DEFINE GAS DENSITY AND VISCOSITY :
C
      RHO=0.0325
      EMU=0.0798
      WRITE(3,1211)RHO
 1211 FORMAT(10X,'DENSITY OF THE GAS IS',E11.4,' LBS/CU FT')
      WRITE(3,1212)EMU
 1212 FORMAT(10X,'VISCOSITY OF THE GAS IS',E11.4,' LBS/HR/FT'/)
C
C          DEFINE GAS VELOCITY
C
      U=30.0
      DO 80 I=1,8
C
C          CALCULATE THE MASS FLOW  (G)
C
      G=RHO*U*3600.0
      WRITE(3,1001)U
 1001 FORMAT( 10X,'GAS VELOCITY (U) IS',F5.0,' FT/SEC')
C
C          CALCULATE REYNOLDS NUMBER (RE)
C
      RE=DIAP*U*RHO/ EMU *3600.
C
C          IF REYNOLDS NUMBER IS LESS THAN 10.0 USE THE FIRST EQUATION.
C          IF REYNOLDS NUMBER IS GREATER THAN  10.0 BUT LESS THEN 200.0
C          USE THE SECOND EQUATION.
C          IF REYNOLDS NUMBER IS GREATER THAN 200.0 USE THE THIRD EQUATION
C
      IF(RE-10.0)30,40,40
C
   30 CONTINUE
      WRITE(3,100)RE
  100 FORMAT(  10X,'LAMINAR FLOW INDICATED BY REYNOLDS NUMBER OF',E12.5)
      DP=200.0*G*EMU*AL*ELMDA**2*(1.0-DELTA)**2
      DP=DP/(SG*DIAP**2*RHO*DELTA**3)
      DP=DP/144.0
      DP=DP/AL
      GO TO 90
C
   40 IF(RE-200.0)50,50,60
C
   50 CONTINUE
      WRITE(3,200)RE
  200 FORMAT(  10X,'TRANSITIONAL FLOW INDICATED BY REYNOLDS NUMBER OF',E
     112.5)
      REMOD=ALOGT(RE)
      EN=0.522*REMOD+0.48187
      F=10.0**(-0.62*REMOD+1.6428)
      DP=2.0*F*G**EN*AL*ELMDA**(3.0-EN)*(1.0-DELTA)**(3.0-EN)
      DP=DP/(DIAP**(3.0-EN)*SG*RHO*DELTA**3)
      DP=DP/144.0
      GO TO 90
```

```
C
   60 CONTINUE
      WRITE(3,300)RE
  300 FORMAT(  10X,'TURBULENT FLOW INDICATED BY REYNOLDS NUMBER OF',E12.
     15)
      DP=0.0243*G**1.9*EMU**0.1*FLMDA**1.1*(1.0-DELTA)
      DP=DP/(DIAP**1.1*SG*RHO*DELTA**3)
      DP=DP/144.0
C
   90 CONTINUE
      WRITE(3,400)DP
  400 FORMAT(  10X,  'DEL P=',E13.5,' PSI/FT'/)
C
      U=U+10.0
   80 CONTINUE
      WRITE(3,1112)
 1112 FORMAT('1')
   70 CONTINUE
      CALL EXIT
      END
```

APPENDIX III REFERENCES

1. Leva, M., et al, "Introduction to Fluidization," Chemical Engineering Progress, Vol. 44, No. 7, p. 518.
2. Ibid, p. 519.
3. Foust, A. S., et al, "Principles of Unit Operations," J. Wiley and Sons, Inc., New York, 1962, p. 476.

APPENDIX IV

REACTOR DESIGN

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APPENDIX IV

REACTOR DESIGN

Optimum design of the catalytic reactor was based on minimum total capita- and operating costs, which are functions of the costs of the reactor, fan, and power calculated on a yearly basis.

Total Cost of Reactor = annual cost of (reactor+fan+power)

The total catalyst volume was fixed by the reaction rate, determined experimentally, for 90% conversion of sulfur dioxide to sulfur trioxide. Consequently, for a given reactor diameter, the height of the catalyst bed is prescribed. It then becomes a matter of determining the most economic geometry for the requisite catalyst volume. If, for example, a given reactor diameter, or cross sectional area of the catalyst bed is increased, the installed cost of the reactor increases; but, due to a corresponding reduction in bed height, the pressure drop decreases, reducing the cost of fan and power. An economic balance shows that at one particular equivalent diameter, the reactor cost is minimum. An increase beyond this point raises cost of the reactor much faster than it lowers the cost of fan and power. Hence, this represents the point of optimum reactor design.

The assumption employed in the optimization program for the large new power plant facility were:

1) Flue gas rate: 2.5 MM SCFM

2) Flue gas temperature: 850°F

3) Total volume of catalyst: 20,000 ft^3

4) Power cost: $0.006/KWH

5) Installed cost of reactor: $2,500/ft (for 30-ft diameter)

6) Installed cost of fan in $: 85.8 ($x^{0.699}$), where x = drive horsepower

7) Depreciation rate for reactor and fan: 10 years, straight line depreciation

The design parameters for the reactor installation for a 1400 MW station, based on our optimization study are:

1) Number of reactors in parallel: 4

2) Number of catalyst beds in parallel in each reactor: 13

3) Height of each bed: 6-1/4 in.
4) Height of each segment: 9 ft.
5) Overall height of each reactor: 117 ft.
6) Diameter of each reactor: 30 ft.
7) Size and shape of catalyst: 3/8 in. cylinders
8) Total pressure drop: 0.96 in. H_2O
9) Total cross sectional area of catalyst: 38,000 sq. ft.
10) Superficial gas velocity through each bed: 3.22 ft/sec.

The computer program for optimum reactor design is shown in Table 39 .

Table 39

```
     PROGRAM DOPT - CALCULATES THE OPTIMUM DIAMETER OF A REACTOR BED.

      REAL KW
      DIMENSION Z(20),IN(10)
      PI=3.1416

      INITIALIZATION OF PARAMETERS FOR BED

   10 CALL READP(6,Z,IN)
      J=IN(1)
      CKW=Z(1)
      TOTV=Z(2)
      D=Z(3)
      THETA=Z(4)
      DD=Z(5)

      INITIALIZATION OF GAS PARAMETERS

   20 CALL READP(5,Z,IN)
      TF=Z(1)
      EMU=Z(2)
      GM=Z(3)
      AMW=Z(4)
      P=Z(5)
      TR=TF+460.
      RHO=AMW*P/(10.72*TR)
      I=0

      PRINT INITIAL PARAMETERS

   30 WRITE(3,500)J,CKW,TOTV,D,DD, THETA,RHO,EMU,GM,TF,AMW,P

      WRITE(3,510)
   35 XSECT=PI*D** 2./4.
      H=TOTV/XSECT
      GUX=GM/XSECT

      CALCULATE THE COST OF THE REACTOR

      VS=PI*15.**2.*H
      SEGM=AINT(TOTV/VS)+1.
      IF(H-8.0)38,38,36
   36 CSTR=14.3*30.*H*SEGM
      GO TO 39
   38 CSTR=2000.*SEGM

      CALCULATION OF PRESSURE DROP

   39 CALL PDROP(J,RHO,EMU,GUX,RE,DP)
      DP=DP*H/144.

      CALCULATE COSTS OF POWER AND FAN AND TOTS

      DAP=2.602E4*DP
      CSTF=85.8*DAP**0.699
      KW=1.940E4*DP
      CSTP=THETA*CKW*KW
      CSTOT=CSTR+CSTF+      CSTP
      WRITE(3,520)XSECT,SEGM,CSTF,CSTP,CSTR,CSTOT,    H    ,DP
   40 CALL DATSW(1,K)
      GO TO (60,50),K
   50 D=D+DD
      GO TO 35
   60 GO TO 10
  500 FORMAT(1H1,3X,'J='I2,2X,'COST/KWH='F9.5,2X'TOT. VOL.='E12.4,2X
     1'DIAM.='E12.5,2X'DD='E12.5,2X'THETA='E12.5//3X,'RHO='E12.5,2X'MU='
     2E12.5,2X,'MASS VEL.='E12.5,2X'TF='F8.2,2X'MW='F8.2,2X'P='F10.4//)
  510 FORMAT(T6'XSECT'T20'SEGM'T34'CSTF'T48'CSTP'T62'CSTR'T76'CSTOT'T90
     1' H'T104'DELT.P'/)
  520 FORMAT(9(2X,E12.5))
      END
```

APPENDIX V

RELATIONSHIP OF W/F FACTORS AND SPACE VELOCITY

APPENDIX V

RELATIONSHIP OF W/F FACTORS AND SPACE VELOCITY

W = catalyst weight, g

d_c = catalyst density, g/liter

L_c = liters of catalyst

v = total gas flow, cc/sec

V = total gas flow, liters/sec = $v \times 10^{-3}$

V' = SO_2 flow, liters/sec

N = moles total gas/sec

n = moles SO_2/sec

P = total pressure, atm.

T = temperature, °K

R = gas constant = 0.082 liter atm/mole-°K

fSO_2 = fraction SO_2, mole or volume = $\frac{V'}{V}$

S = space velocity, sec^{-1} = liters SO_2/liter catalyst - sec = $\frac{V'}{L_c}$

Convert W/F, g-sec/cc total gas flow, $Q_1 = \frac{W}{v}$

to W/F, g-sec/mole SO_2, $Q_2 = \frac{W}{n}$

(1) $V = v \times 10^{-3}$

(2) $N = \frac{PV}{RT}$

(3) $n = f_{SO_2} (N) = \frac{f_{SO_2} PV}{RT}$

for out test system: $P = 1$ atm

$T = 25°C\ (298°K)$

$$(4) \quad n = \frac{f_{SO_2}\ (V)}{(0.082)(298)} = \frac{f_{SO_2}\ (v)}{24.5 \times 10^3}$$

then

$$(5) \quad Q_2 = \frac{W(24.5 \times 10^3)}{v\ (f_{SO_2})} = \frac{24.5 \times 10^3\ Q_1}{f_{SO_2}}$$

Convert Q to S.

For the general case:

$$(6) \quad Q_2 = \left(\frac{RT}{P}\right) \frac{Q_1}{f_{SO_2}} \times 10^3 = \frac{W(RT)}{f_{SO_2}\ (PV)}$$

but $W = d_c L_c$

and $f_{SO_2} = \frac{V'}{V}$

$$(7) \quad Q_2 = \frac{d_c L_c (RT)}{\frac{V'}{V}\ (PT)} = \frac{d_c L_c (RT)}{V'\ (P)} = d_c \left(\frac{RT}{P}\right)\left(\frac{1}{S}\right)$$

and

$$(8) \quad S = \frac{d_c}{Q_2} \left(\frac{RT}{P}\right)$$

APPENDIX VI

COMPARATIVE COST OF PLATINUM AND VANADIA CATALYSTS

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APPENDIX VI

COMPARATIVE COST OF PLATINUM AND VANADIA CATALYSTS

The literature fails to reveal catalysts for this application better than vanadia or platinum, which are about equivalent in conversion efficiency. The possibility cannot be ignored that a better catalyst may be announced at any time in the future. Nevertheless, at the moment, there are only the two cited. A cost analysis of platinum and vanadia catalysts summarized, in Table 40, indicates that the platinum catalyst must be at least ten times as effective as vanadia catalyst to be comparable in cost with vanadium catalyst. Decrease in platinum catalyst cost is not expected in the near future because platinum and labor costs are increasing.

Table 40

SUMMARY OF ECONOMICS FOR VANADIA AND PLATINUM CATALYSTS(3)

	V Catalyst	Pt Catalyst
Volume, Cu ft(1)	30,300	3,020
Initial cost, dollars(2)	1,250,000	12,800,000
Regeneration cost, dollars(2)	---------	1,032,000
Capitalized cost, dollars(2)	3,920,000	20,380,000

NOTES: (1) Estimate of the volume of platinum catalyst that would be equal in cost to the estimated cost of vanadia catalyst.

(2) Estimates are based on the same W/F ratio for platinum and vanadia catalysts.

(3) Assumptions used for comparison of platinum and vanadia catalysts:

General:

a. rate of return: 8% per year

Vanadia Catalyst:

b. amount used for the oxidation of SO_2 in flue gas: 30,300 ft^3

c. price: \$41/ft^3

d. packed density: 36.8 lb/ft^3

e. catalyst life: 5 years

Platinum Catalyst:

f. catalyst contains 0.5% platinum

g. packed density: 50 lb/ft^3

h. catalyst cost: cost of platinum + \$2.75/lb catalyst, (for manufacturing cost)

i. regeneration cost: \$0.75/lb catalyst

j. regeneration interval: 2 years

k. loss of platinum during regeneration: 2%

l. price of platinum: \$110/oz (troy)

m. catalyst life: 30 years (including obsolescence and/or abandonment)

(1) To estimate the volume of Pt catalyst that would equal in cost the cost of vanadia catalyst required for a particular flue gas application.

Initial cost of vanadia catalyst

$$= 860{,}000 \text{ liters} \times \frac{\$1.45}{\text{liter}}$$

$$= \$1{,}250{,}000$$

Capitalized cost for vanadia catalyst

$$= \$1{,}250{,}000 \times \left[\frac{(1+0.08)^5}{(1+0.08)^5-1}\right]$$

$$= \$1{,}250{,}000 \times 3.131$$

$$= \$3{,}920{,}000$$

Assuming that the amount of Pt catalyst required = P lb

Initial cost of Pt catalyst,

$$A = \text{Cost of Pt} + \text{manufacturing cost of Pt catalyst}$$

$$= 0.005 \text{ P lb} \times \frac{\$1760}{\text{lb}} + \frac{\$2.75}{\text{lb}} \times \text{P lb}$$

$$= 8.8P + 2.75P$$

$$= 11.55P$$

Regeneration cost of Pt catalyst:

$$H = \text{Refining cost} + \text{cost of Pt loss}$$

$$= \frac{\$0.75}{\text{lb}} \times P\ \text{lb} + 0.0001 \times P\ \text{lb} \times \frac{\$1760}{\text{lb}}$$

$$= 0.75P + 0.176P$$

$$= 0.926P$$

To calculate the volume of Pt catalyst, capitalized cost of vanadium catalyst = capitalized cost of initial Pt catalyst + capitalized cost of regenerating Pt catalyst every two years

$$3{,}920{,}000 = AF_{30} + H\ (G_2 - G_{30})$$

$$= 11.55P \left[\frac{(1+0.08)^{30}}{(1+0.08)^{30}-1}\right] + 0.926P \left[\frac{1}{(1+0.08)^{2}-1} - \frac{1}{(1+0.08)^{30}-1}\right]$$

$$= 11.55P \times 1.110 + 0.926P\ (6.010 - 0.1103)$$

$$= 11.55P \times 1.110 + 0.926P \times 5.8997$$

$$= 18.283P$$

$$P = 151{,}000 \text{ lb of Pt catalyst}$$

$$= 3{,}020 \text{ cu ft of Pt catalyst}$$

(2) at same W/F values of Pt and V catalysts, what weight of Pt catalyst is required? Cost of Pt catalyst? Cost of V catalyst?

$$\text{Weight of V catalyst} = 30{,}300\ \text{ft}^3 \times \frac{36.8\ \text{lb}}{\text{ft}^3}$$

$$= 1{,}115{,}000\ \text{lb}$$

$$= 505 \times 10^6\ \text{gm}$$

$$\text{Weight of Pt catalyst} = 1{,}115{,}000\ \text{lb}$$

$$SO_2 = 150 \times 10^6\ \text{SCFH} \times 0.003$$

$$= 0.45 \times 10^6\ \text{SCFH}$$

$$= 0.45 \times 10^6\ \frac{\text{SCF}}{\text{Hr}} \times \frac{\text{Hr}}{3600\ \text{sec}} \times \frac{\text{lb-mole}}{379\ \text{SCF}} \times 454\ \frac{\text{g}}{\text{lb}}$$

$$= \frac{204 \times 10^6}{136 \times 10^4} = 1.5 \times 10^2\ \frac{\text{mole}}{\text{sec}}$$

$$W/F = 505 \times 10^6\ \text{g} \times \frac{\text{sec}}{1.5 \times 10^2\ \text{mole}\ SO_2}$$

$$= 3.37 \times 10^6\ \frac{\text{g-sec}}{\text{mole}\ SO_2}$$

Initial cost of V catalyst = $1,250,000

Capitalized cost = $3,920,000

Initial cost of Pt catalyst,

= Cost of Pt + Manufacturing cost of of Pt catalyst

$$= 0.005 \times 1{,}115{,}000 \text{ lb} \times \frac{\$1760}{\text{lb}} + \frac{\$2.76}{\text{lb}} \times 1{,}115{,}000 \text{ lb}$$

$$= \$12{,}880{,}000$$

Regeneration cost of Pt catalyst

= Refining cost + cost of Pt loss

$$= \frac{\$0.75}{\text{lb}} \times 1{,}115{,}000 \text{ lb} + 0.0001 \times 1{,}115{,}000 \text{ lb} \times \frac{\$1760}{\text{lb}}$$

$$= \$1{,}032{,}000$$

Capitalized cost of Pt catalyst

$$= \$12{,}880{,}000 \times 1.110 \times \$1{,}032{,}000 \times 5.8997$$

$$= \$20{,}380{,}000$$

APPENDIX VII

SORPTION ISOTHERMS FOR MOLECULAR SIEVES

APPENDIX VII

SORPTION ISOTHERMS FOR MOLECULAR SIEVES

Molecular sieves have recently been shown to be useful in many applications as heterogeneous catalysts and as vehicles in studies of catalysts and catalyst mechanisms. However, no publication, to our knowledge, has revealed specific studies to determine their merit as support material for known SO_2 oxidation catalysts.

We obtained samples of several experimental forms of zeolite materials and embarked upon a program to screen the materials as potential supports. The monodisperse nature of the zeolite pores and their extremely high specific area are characteristics highly favorable for maximum contact conditions between the SO_2 and active catalyst.

Zeolite materials are well known for their adsorption characteristics with regard to the various constituents in stack gas, and we wished to know if these characteristics would be an aid or hindrance in our contemplated use of them as a support material. Initial experiments were performed at a low temperature range (75° to 250°F) as shown in Figures 55 through 61.

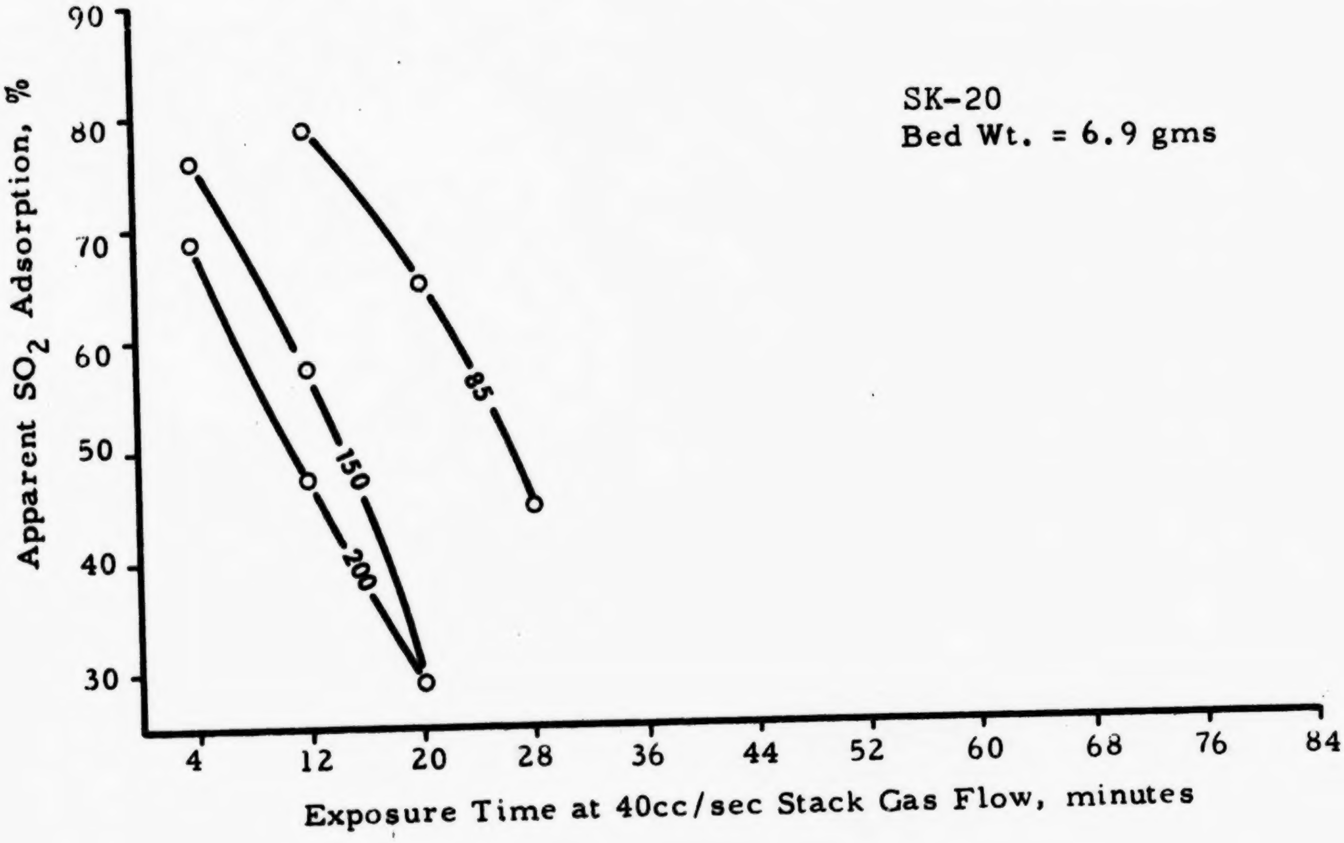

Figure 55. Sorption for Molecular Sieve SK-20

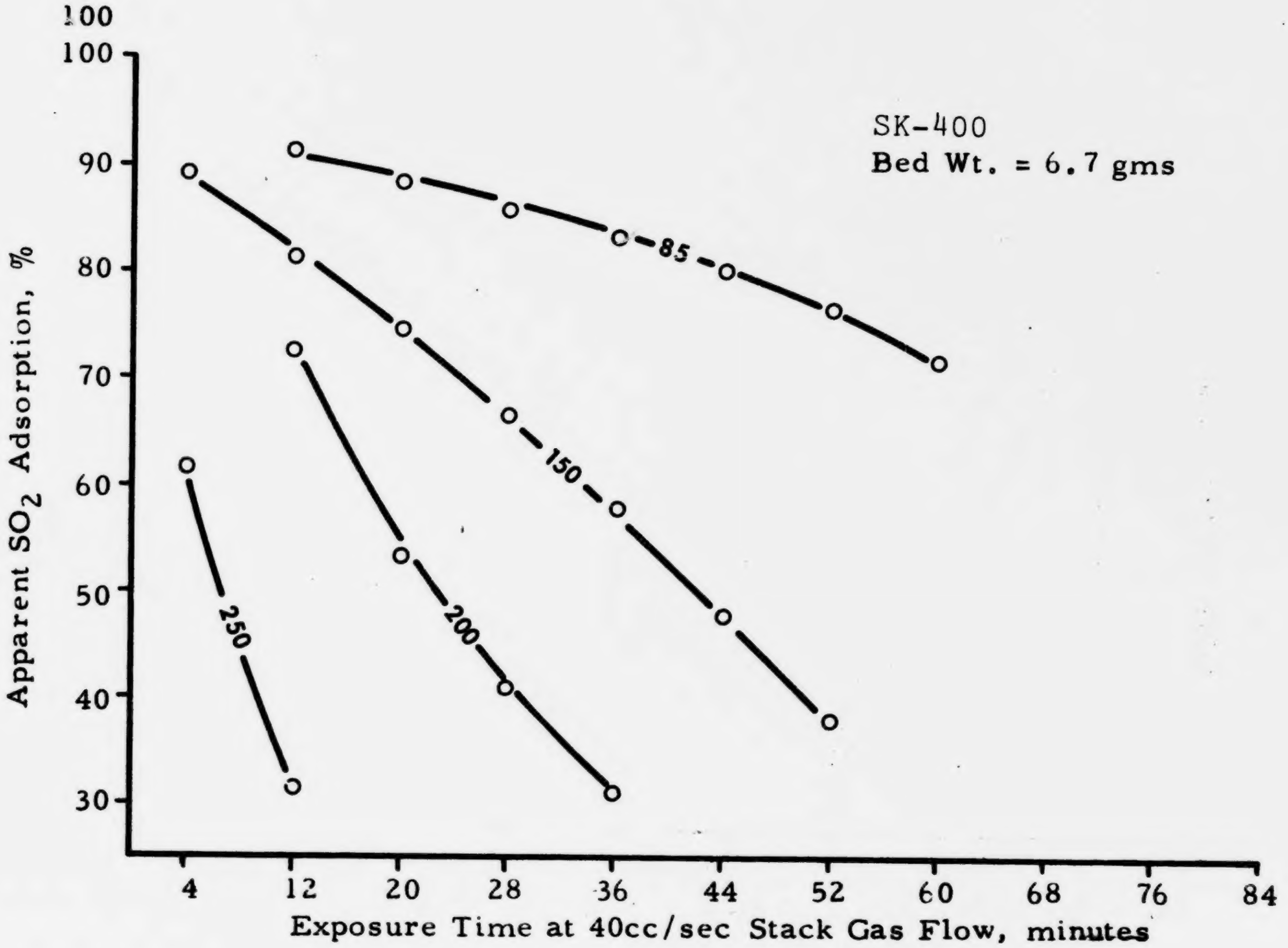

Figure 56. Sorption Isotherms for Molecular Sieve SK-400

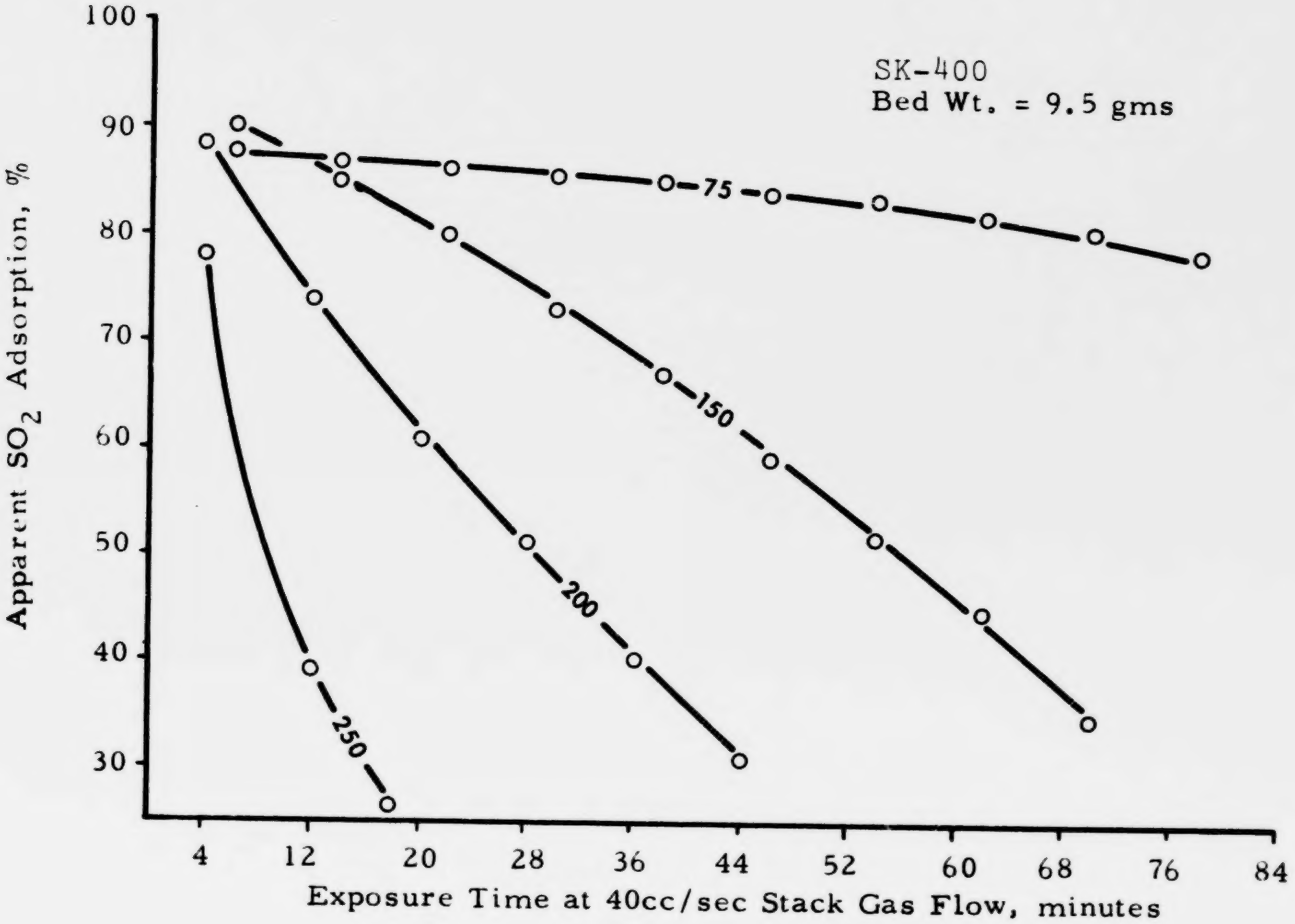

Figure 57. Sorption Isotherms for Molecular Sieve SK-400

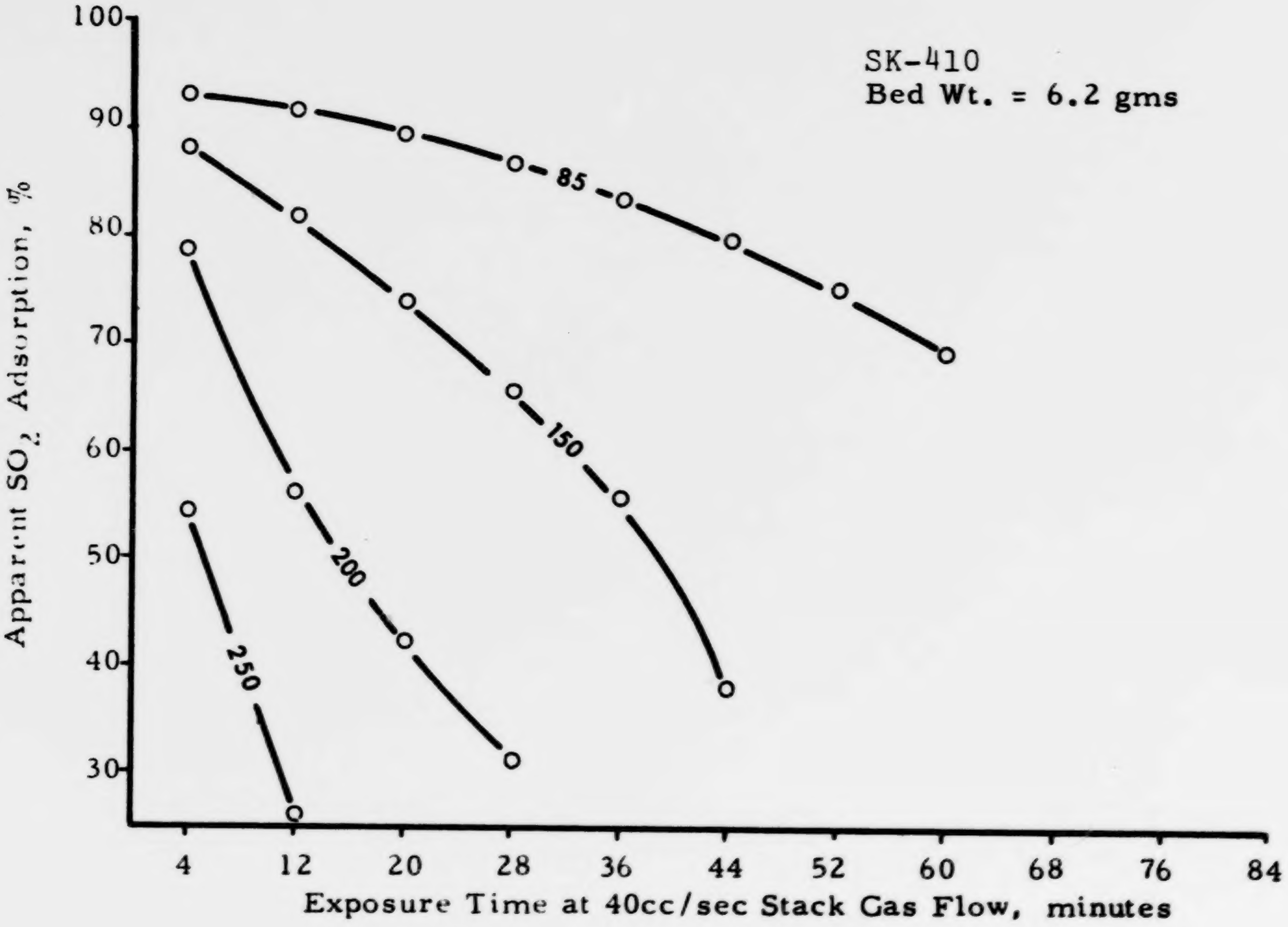

Figure 58. Sorption Isotherm for Molecular Sieve SK-410

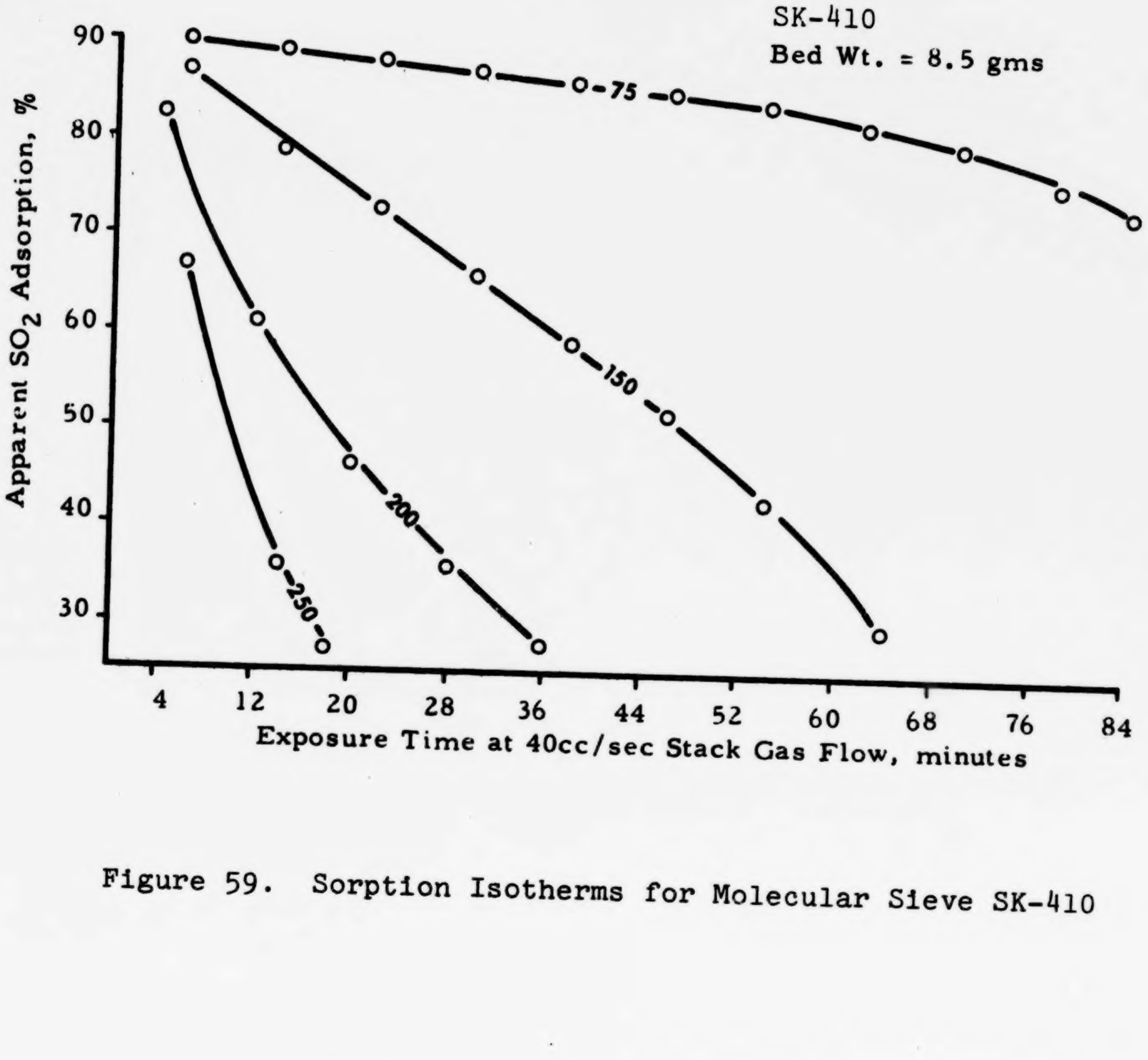

Figure 59. Sorption Isotherms for Molecular Sieve SK-410

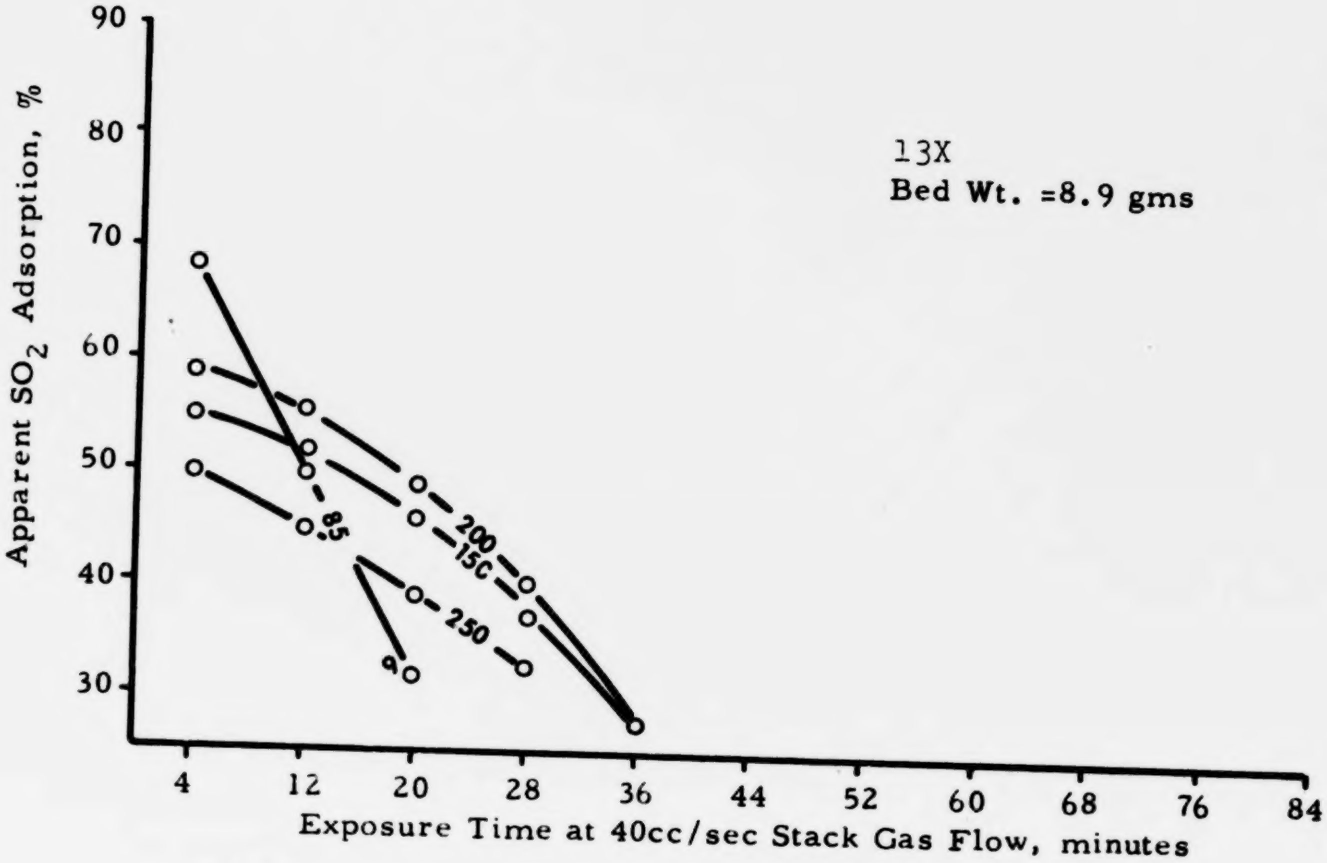

Figure 60. Sorption Isotherms for Molecular Sieve 13X

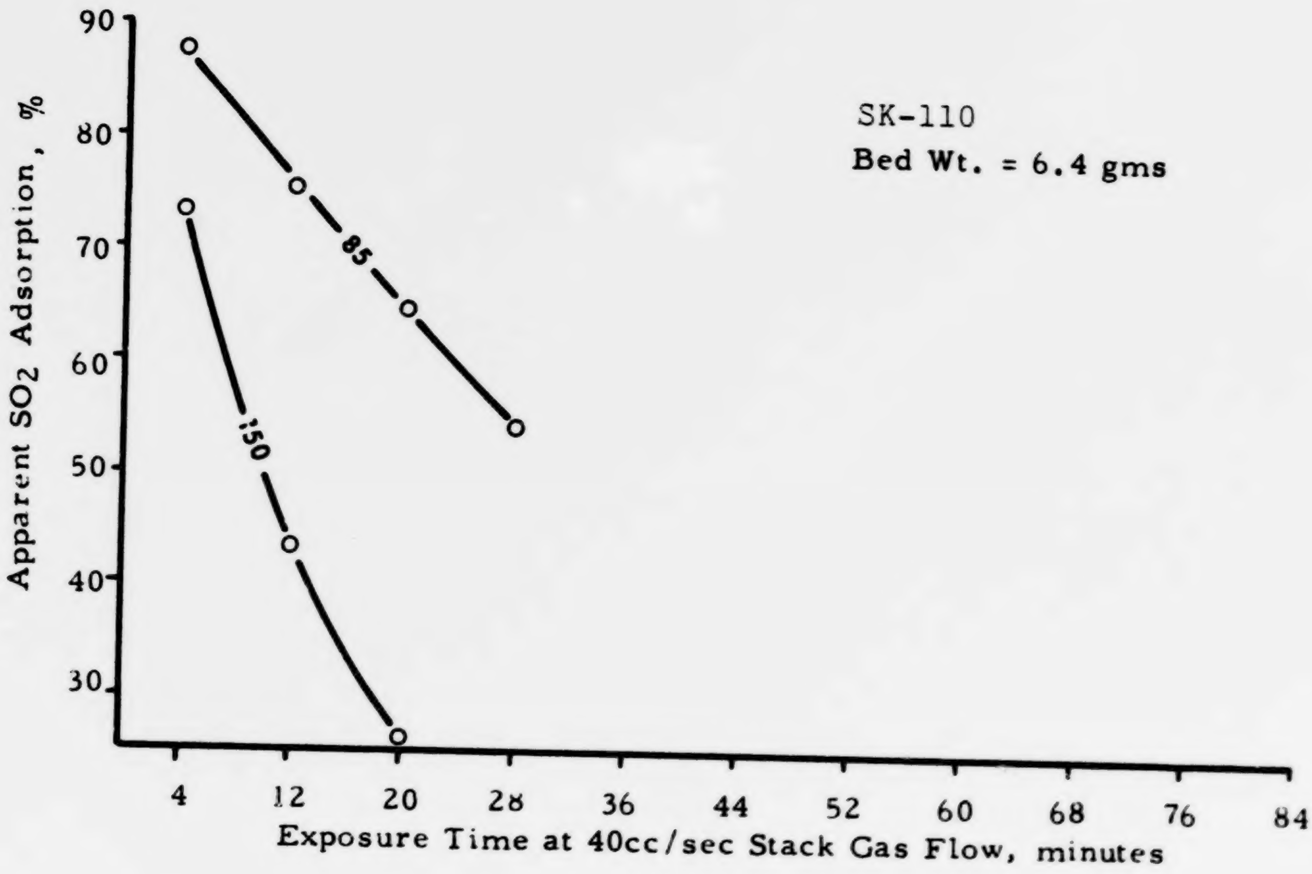

Figure 61. Sorption Isotherms for Molecular Sieve SK-110

APPENDIX VIII

TYCO MODIFIED CHAMBER PROCESS REPORT

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APPENDIX VIII

TYCO MODIFIED CHAMBER PROCESS FOR REMOVAL OF SO_2 FROM POWER PLANT FLUE GAS *

The basic reactions which describe both the Lead Chamber Process for sulfuric acid manufacture and the basic Tyco Modified Chamber Process are shown on page 175. Sulfur dioxide is oxidized with excess nitrogen dioxide and water to form sulfuric acid and equimolar quantities of nitric oxide and nitrogen dioxide (1 and 2) which are absorbed in sulfuric acid forming nitrosylsulfuric acid (3). The oxides of nitrogen are recovered by heating the $HNSO_5$ after which the NO is reoxidized to NO_2 (4). In the Tyco Process, excess NO_2 is absorbed in water forming nitric acid (5).

The flow sheet in Figure 62 shows the basic difference between the standard Lead Chamber Process and the Tyco Modified Process. In the standard process the NO is present in high enough concentrations to allow the reoxidation to take place in the same reaction mixture as the SO_2 oxidation. In the new process, the NO is too dilute to allow the slow oxidation to occur in reasonable contact times, thus requiring the concentration of the NO and separate oxidation.

The process as shown in Figure 62 is profitable, but suffers from the disadvantage of requiring 37% additional coal to provide the necessary energy. The heat is needed to (1) vaporize the NO and NO_2 for recycling, and (2) to concentrate the acid back to 80% for recycle.

In trying to overcome these deficiencies, two major breakthroughs in process concept have been achieved which may well make the Modified Chamber Process a practical one for removing SO_2 from power plant flue gas and may have a profound effect on the sulfuric acid manufacturing industry in general.

Figure 63 shows an Isothermal Scrubber in which the gas is scrubbed with hot sulfuric acid. The entering hot acid has an equilibrium vapor pressure of water such that all the water that comes in with the raw flue gas leaves with the clean stack gas. The bottom of the scrubber is also run at conditions such that there is no net transfer of water between gas and liquid.

To accelerate the recovery and reoxidation of the oxides of nitrogen we examined the stepwise reactions on page 178. The third equation shows that the net reaction is an oxidation of $HNSO_5$ which might well be carried out in the liquid phase. This reaction does not occur by simply contacting air with $HNSO_5$ solution (in H_2SO_4), but we have found that by using an activated carbon catalyst, the reaction does take place. Experimental results comparing charcoal-

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*Report presented by Tyco at June 11-13, 1969 Contractors meeting.

catalyzed and uncatalyzed reactions are shown on page 179. Figure 64 shows the proposed catalytic stripper which takes advantage of the greatly accelerated NO_2 recovery.

These two modifications lead to the simplified Catalytic Chamber Process shown in Figure 65. The important thing to note is that no additional heat energy is required above that which comes in with the flue gas at 300°F.

The sulfuric acid concentration in the recycle (product) stream of the newly modified system is no longer limited by equilibrium of vapor pressure considerations as it was in the original Chamber Process. It is only limited by the loss of H_2SO_4 vapor at the temperatures required to permit the water vapor to escape with the stack gas. This places a limit of 92% H_2SO_4 on the power plant flue gas cleaning process, but does not impose the same limit on the Lead Chamber Process which does not have the problem of water removal. Acid at 100% concentration could conceivably be produced in this simpler Lead Chamber Process using catalytic stripping techniques.

This removal of the additional heat requirements greatly improves the economics of the system as shown on pages 182 and 183. Use of the NAPCA guidelines for the catalytic process have raised the total capital cost and general operating cost estimates to somewhat higher levels than the more liberal estimates for the baseline process, but the dramatic difference lies in the saving on heat and cooling water. This saving amounts to more than $6 million in annual operating expenses. Using credits shown on page 183, we estimate the process to earn $2.62 per ton of coal or 39.5% return on capital investment making the process both technically and economically attractive.

PROCESS REACTIONS

(1) $SO_2 + 2NO_2 \longrightarrow SO_3 + NO + NO_2$

(2) $SO_3 + H_2O \longrightarrow H_2SO_4$

(3) $NO + NO_2 + 2H_2SO_4 \longrightarrow 2HNSO_5 + H_2O$

(4) $2NO + O_2 \longrightarrow 2NO_2$

(5) $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$

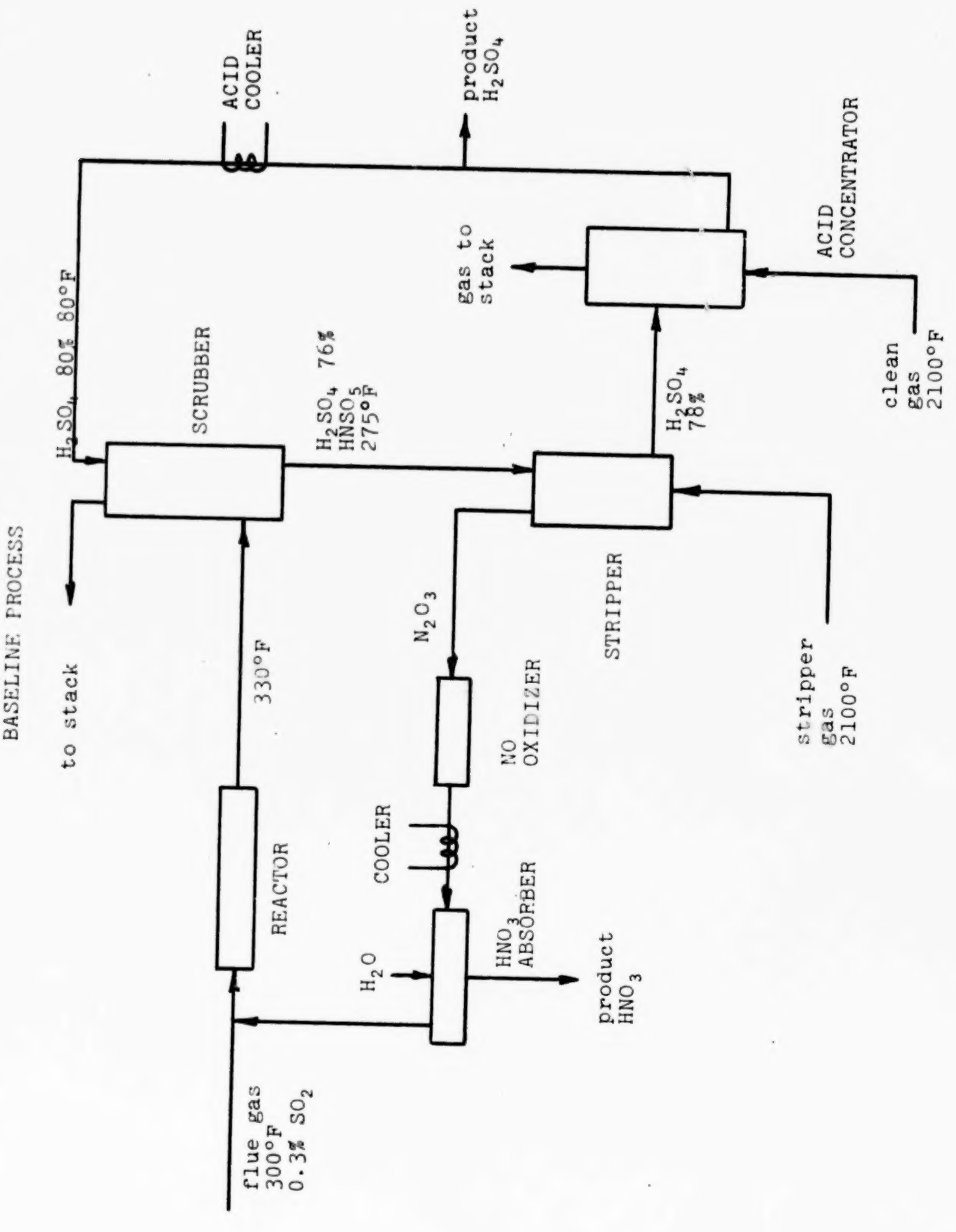
BASELINE PROCESS
to stack
H_2SO_4 80% 80°F
SCRUBBER
ACID COOLER
product H_2SO_4
gas to stack
ACID CONCENTRATOR
clean gas 2100°F
H_2SO_4 78%
H_2SO_4 76% $HNSO_5$ 275°F
STRIPPER
stripper gas 2100°F
N_2O_3
NO OXIDIZER
COOLER
HNO_3 ABSORBER
product HNO_3
H_2O
REACTOR
330°F
flue gas 300°F 0.3% SO_2

Figure 62

ISOTHERMAL SCRUBBER

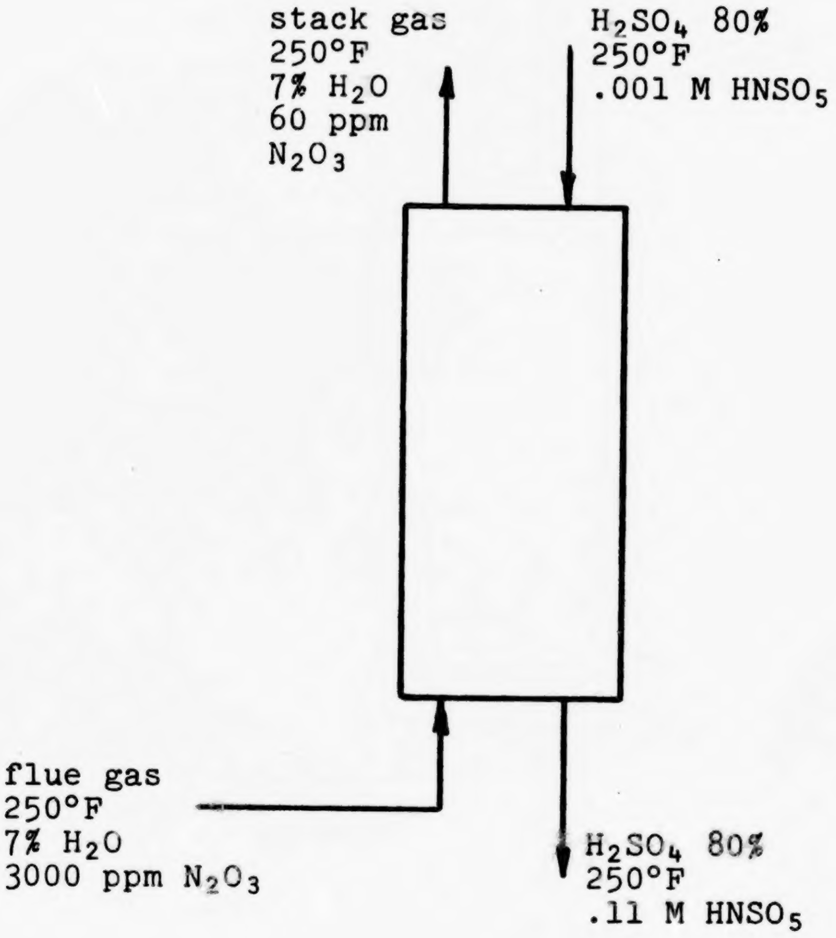
stack gas
250°F
7% H_2O
60 ppm
N_2O_3
H_2SO_4 80%
250°F
.001 M $HNSO_5$
flue gas
250°F
7% H_2O
3000 ppm N_2O_3
H_2SO_4 80%
250°F
.11 M $HNSO_5$

Figure 63

NITROSYLSULFURIC ACID OXIDATION

$$4HNSO_5 + 2H_2O \longrightarrow 2N_2O_3 + 2H_2SO_4$$

$$2N_2O_3 + O_2 \longrightarrow 4NO_2$$

$$4HNSO_5 + O_2 + 2H_2O \longrightarrow 4NO_2 + 4H_2SO_4$$

NITROSYLSULFURIC ACID OXIDATION EXPERIMENTS

Carrier Gas	Packing	Concentration (mm Hg)	
		NO	NO_2
Nitrogen	Saddles	0.01	0.01
Air	Saddles	0.01	0.02
Air	Charcoal	0.01	0.75

CATALYTIC STRIPPER

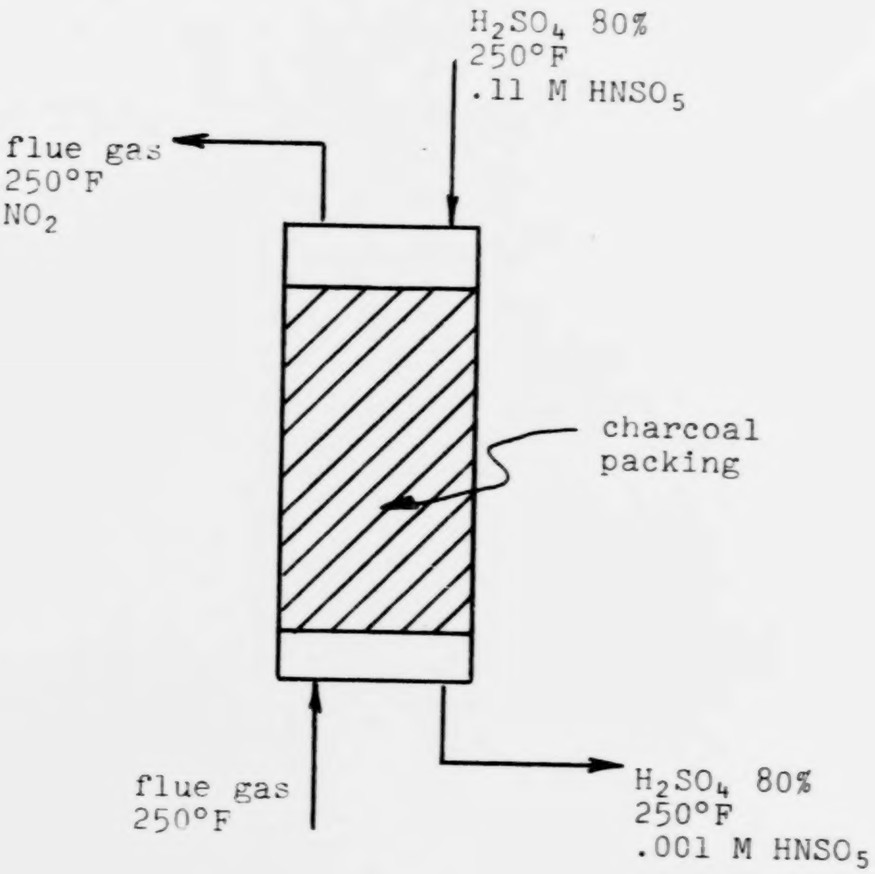
H_2SO_4 80%
250°F
.11 M $HNSO_5$
flue gas
250°F
NO_2
charcoal packing
flue gas
250°F
H_2SO_4 80%
250°F
.001 M $HNSO_5$

Figure 64

CATALYTIC CHAMBER PROCESS

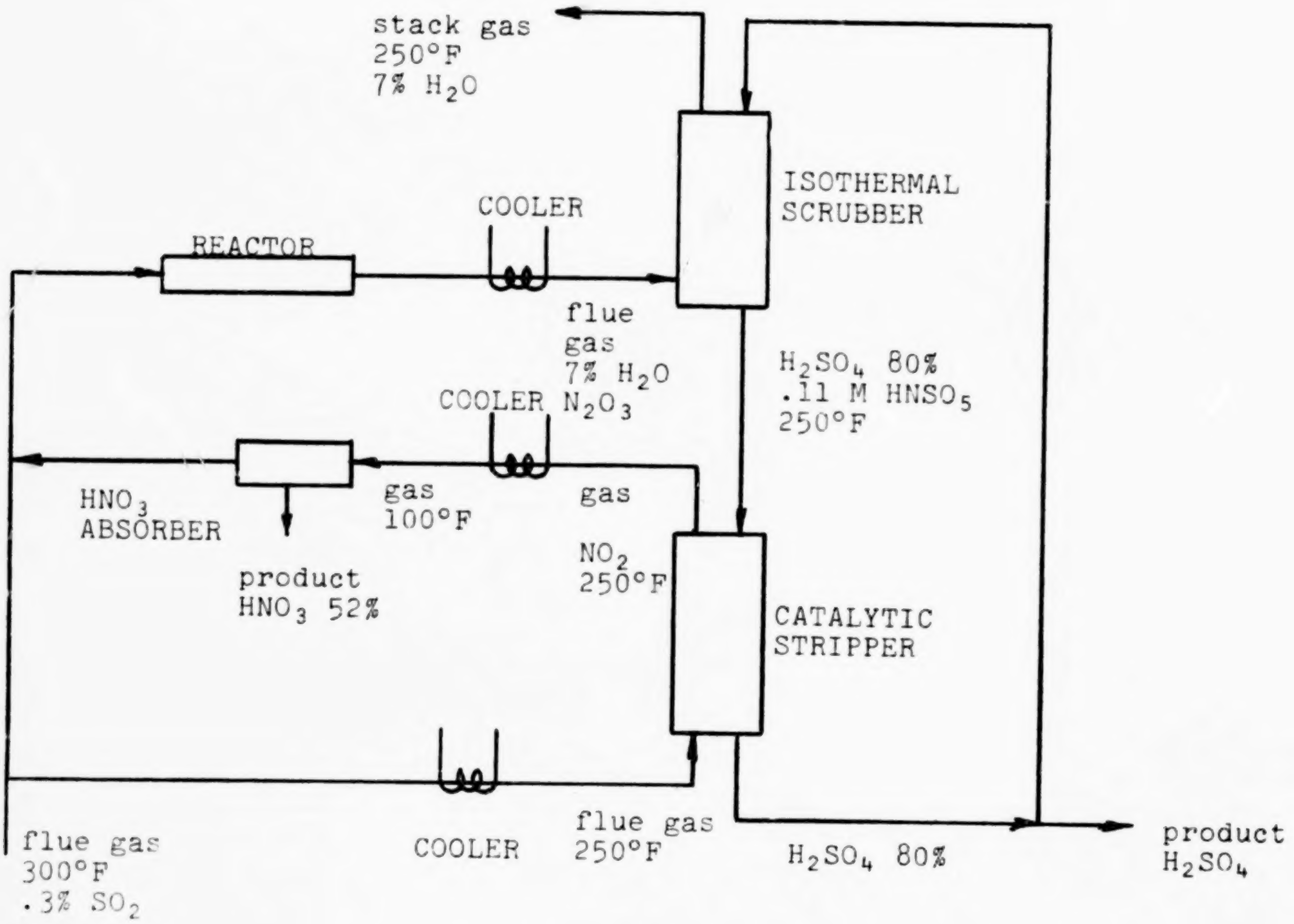
stack gas
250°F
7% H_2O
ISOTHERMAL
SCRUBBER
COOLER
REACTOR
flue
gas
7% H_2O
N_2O_3
H_2SO_4 80%
.11 M $HNSO_5$
250°F
COOLER
HNO_3
ABSORBER
gas
100°F
gas
product
HNO_3 52%
NO_2
250°F
CATALYTIC
STRIPPER
flue gas
300°F
.3% SO_2
COOLER
flue gas
250°F
H_2SO_4 80%
product
H_2SO_4

Figure 65

ECONOMIC ANALYSIS

ITEM	BASELINE PROCESS		CATALYTIC PROCESS
Major equipment	$4,535,000		$ 3,985,000
Total Capital Cost	9,271,000		12,600,000
Annual Operating Cost			
Heat	5,220,000		--
Water	1,133,000		168,000
Total	6,353,000		168,000
Saving (heat and water)		$6,185,000	
Other operating costs	2,159,400		3,688,900
Total operating cost	$8,513,400		$ 3,856,900

	BASELINE PROCESS	CATALYTIC PROCESS
Credits		
H_2SO_4 @ \$20/ton (100%)	\$6,201,000	\$6,201,000
HNO_3 @ \$84/ton (52%)	3,530,000	3,530,000
Total credits	9,731,000	9,731,000
Operating costs	8,513,400	3,856,900
Profit	1,217,600	5,874,100
\$/ton coal	0.55	2.62
Return on Investment	13.1%	39.5%

APPENDIX IX

VAPOR PRESSURE APPARATUS AND PROCEDURES

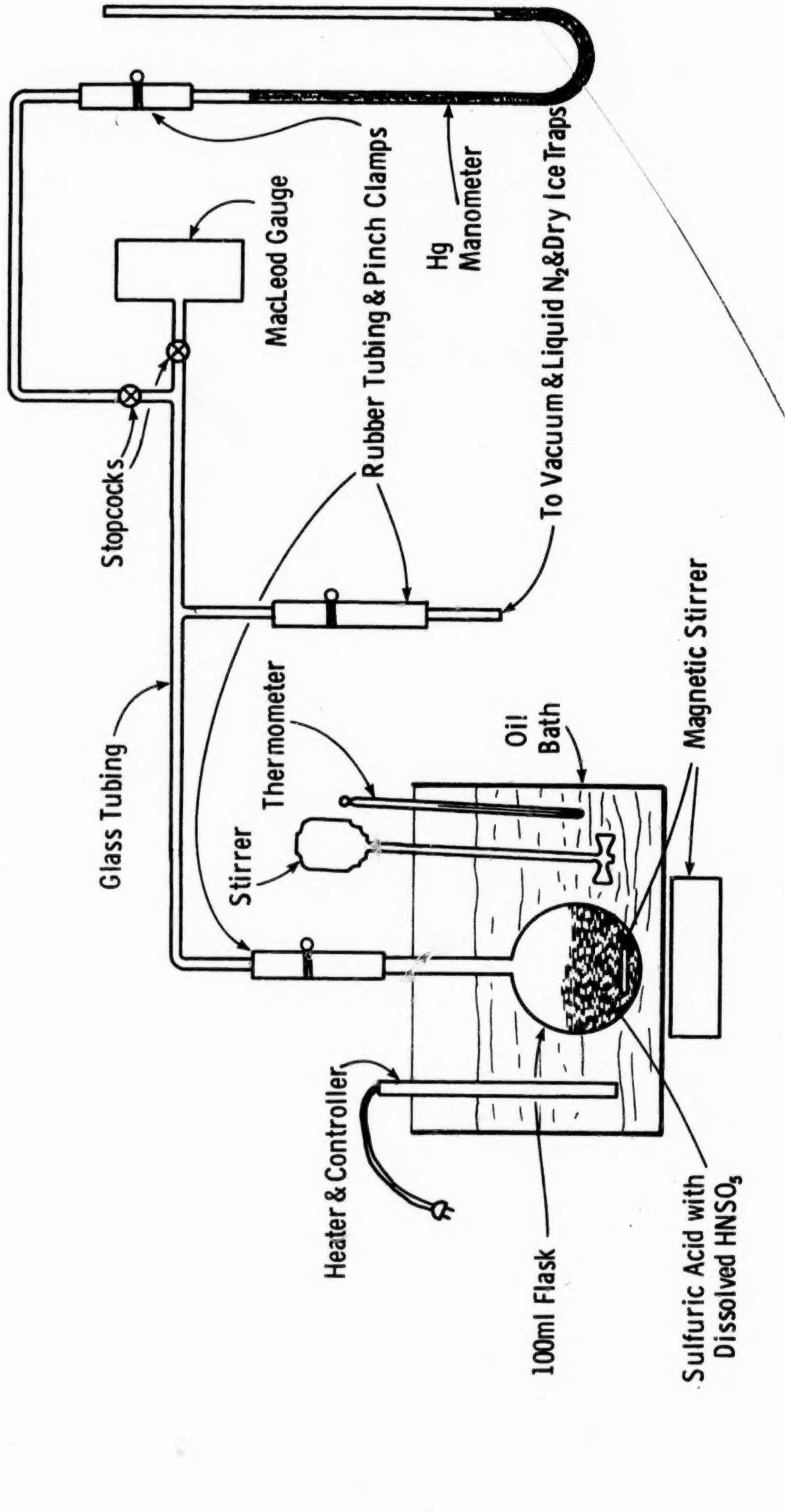
Glass Tubing
Stopcocks
Stirrer
Thermometer
Rubber Tubing & Pinch Clamps
MacLeod Gauge
Heater & Controller
100ml Flask
Oil Bath
To Vacuum & Liquid N_2 & Dry Ice Traps
Hg Manometer
Sulfuric Acid with Dissolved $HNSO_5$
Magnetic Stirrer

Figure 66

APPENDIX IX

PROCEDURE FOR OBTAINING VAPOR PRESSURE DATA

1. A quantity of H_2SO_4 of the desired concentration was weighed and transferred into the 100 ml flask (approx. 50-60 ml).
2. A quantity of anhydrous nitrosylsulfuric acid was weighed and transferred to the flask.

   Formula: $N_2O_3 \cdot (SO_3)_2$

3. The flask containing the above mixture was cooled in an ice bath to approx. 2°C.
4. The flask was connected to the rubber tubing and vacuum was pulled on the system (down to approx. 0.05 mm Hg). This removed dissolved gases in the acid as well as the gases from the vapor space.
5. The pinch clamp above the flask was closed tightly.
6. The flask was then placed in the oil bath and heated to the desired temperature (while stirring).
7. The flask was held at the desired temperature for 1-3 hours. (Until no evidence of gas evolution was observed).
8. The remainder of the system was evacuated to approx. 0.01 mm Hg and the pinch clamp to the vacuum source was closed.
9. The pinch clamp above the flask was opened for about 3 seconds. This is long enough to equalize the pressure throughout the system but not long enough for a significant quantity of vapor to evolve from the solution.

   NOTE: The stirring bar was stopped prior to opening the pinch clamp.

10. The pressure in the manometer was quickly measured and corrected for the ratio of volumes and the temperature difference. The two volumes were (1) the free space above the flask up to the pinch clamp, and (2) the volume from that pinch clamp to the rest of the system including the manometer leg. The temperature of the system was taken as the "weighted" average between the temperature of the oil bath and room temperature.
11. The contribution of water vapor was subtracted from the total corrected pressure.

12. It was assumed that the total pressure (minus H_2O pressure) was a result of equal moles of $NONO_2$. No association of these gases or any other gases was assumed.

The step which proved to be the cause of the erroneous results was step 9. Apparently sufficient vaporization occurs (even with a quiesent liquid) in two-three seconds to cause a "high" vapor pressure reading. This was demonstrated by opening the pinch clamp above the flask and waiting until the entire system was at equilibrium. The final pressure measured at equilibrium differed by about 25% from the pressure measured after two-three seconds exposure to the flask.

APPENDIX X

SO_3-PRODUCT ACID RELATIONSHIPS

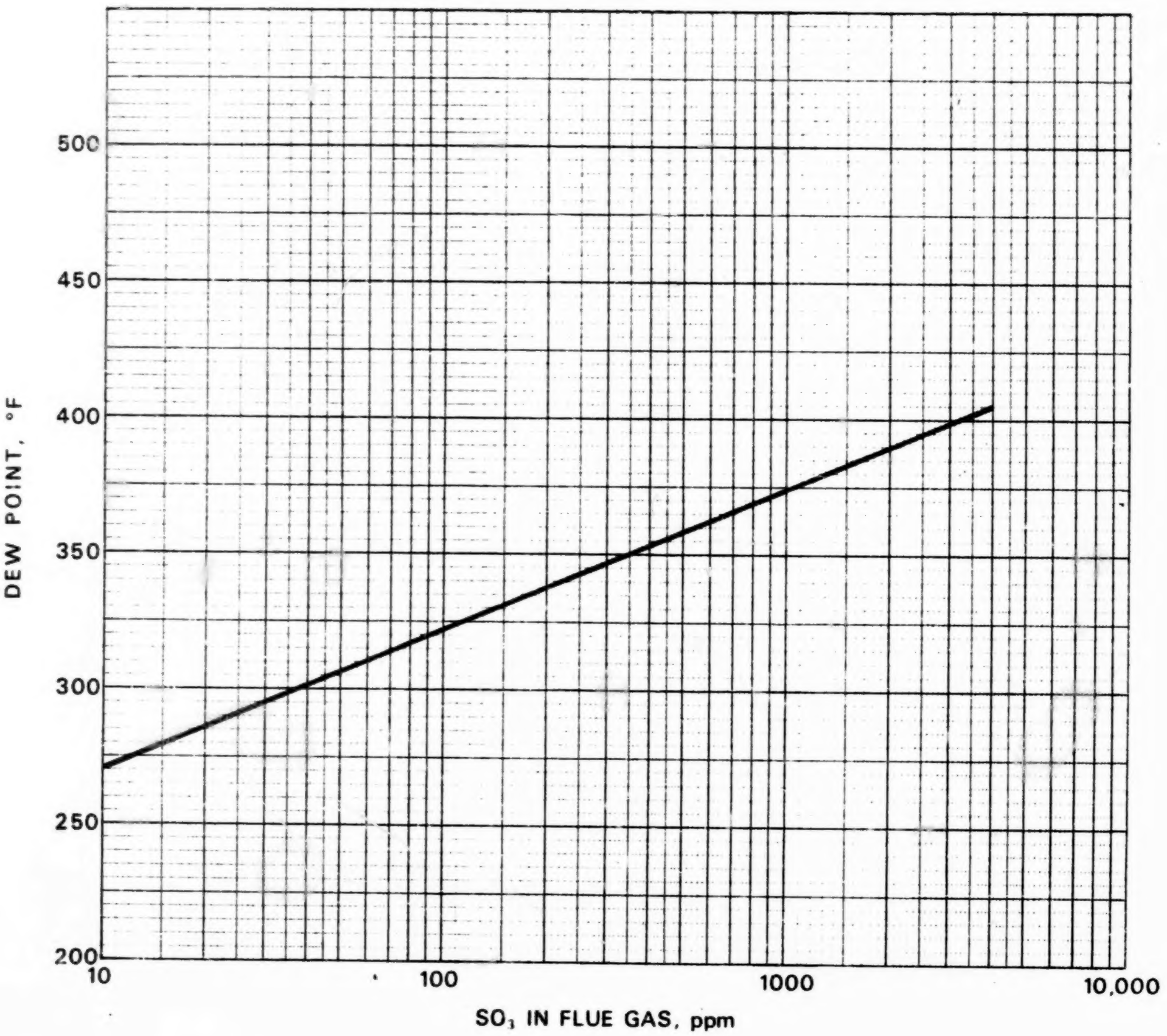

Figure 67. Effect of SO_3 Concentration in Flue Gas on Dew Point of the Acid

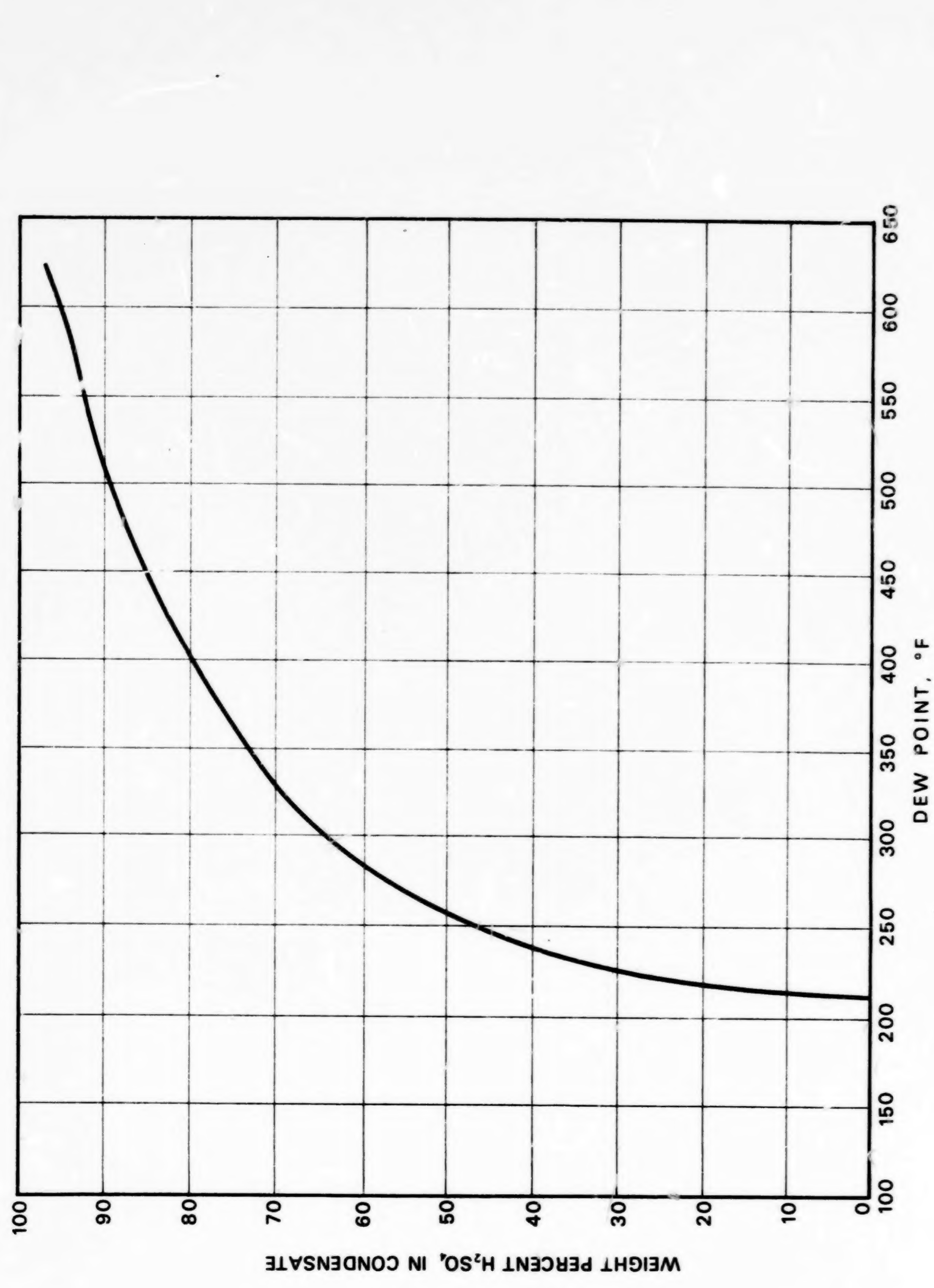

Figure 68. Relationship of Flue Gas Dew Point to Acid Concentration in Condensate